MONOGRAPHS ON INDUSTRIAL CHEMISTRY

Edited by Sir EDWARD THORPE, C.B., LL.D., F.R.S.

Emeritus Professor of General Chemistry in the Imperial College of Science and Technology, South Kensington; and formerly Principal of the Government Laboratory, London.

INTRODUCTION

DURING the last four or five decades the Applications of Chemistry have experienced an extraordinary development, and there is scarcely an industry that has not benefited, directly or indirectly, from this expansion. Indeed, the Science trenches in greater or less degree upon all departments of human activity. Practically every division of Natural Science has now been linked up with it in the common service of mankind. So ceaseless and rapid is this expansion that the recondite knowledge of one generation becomes a part of the technology of the next. Thus the conceptions of chemical dynamics of one decade become translated into the current practice of its successor; the doctrines concerning chemical structure and constitution of one period form the basis of large-scale synthetical processes of another; an obscure phenomenon like Catalysis is found to be capable of widespread application in manufacturing operations of the most diverse character.

This series of Monographs will afford illustrations of these and similar facts, and incidentally indicate their bearing on the trend of industrial chemistry in the near future. They will serve to show how fundamental and essential is the relation of principle to practice. They

will afford examples of the application of recent knowledge to modern manufacturing procedure. As regards their scope, it should be stated the books are not intended to cover the whole ground of the technology of the matters to which they relate. They are not concerned with the technical *minutiæ* of manufacture except in so far as these may be necessary to elucidate some point of principle. In some cases, where the subjects touch the actual frontiers of progress, knowledge is so very recent and its application so very tentative that both are almost certain to experience profound modification sooner or later. This, of course, is inevitable. But even so such books have more than an ephemeral interest. They are valuable as indicating new and only partially occupied territory; and as illustrating the vast potentiality of fruitful conceptions and the worth of general principles which have shown themselves capable of useful service.

The following Volumes have already been arranged for:—

The Scientific Use of Coal. By W. A. Bone, D.Sc., F.R.S., Imperial College of Science and Technology, South Kensington.

Catalysis in Industrial Chemistry. By G. G. Henderson, M.A., D.Sc., LL.D., F.R.S., The Royal Technical College, Glasgow.

Synthetic Colouring Matters: Sulphur Dyes. By G. T. Morgan, D.Sc., A.R.C.S., F.R.S., Finsbury Technical College, London.

Organic Compounds of Arsenic and Antimony. By G. T. Morgan, D.Sc., A.R.C.S., F.R.S., Finsbury Technical College, London.

Synthetic Colouring Matters: Vat Colours. By Jocelyn F. Thorpe, C.B.E., D.Sc., F.R.S., Imperial College of Science and Technology, South Kensington.

Naphthalene. By W. P. Wynne, D.Sc., F.R.S., The University, Sheffield.

Synthetic Colouring Matters: Azo-Dyes. By Francis W. Kay, D.Sc., The University, Liverpool.

Utilisation of Atmospheric Nitrogen: Synthetical Production of Ammonia and Nitric Acid. By A. W. Crossley, C.M.G., D.Sc., F.R.S., F.I.C., King's College, Strand.

Cement. By BERTRAM BLOUNT, F.I.C.

Edible Oils and Fats. By C. A. MITCHELL, B.A., F.I.C.

The Principles and Practice of Gas-purification. By EDWARD V. EVANS, F.I.C., Chief Chemist, South Metropolitan Gas Company.

Refractories. By J. W. MELLOR, D.Sc.

The Applications of Electrolysis in Chemical Industry By ARTHUR J. HALE, B.Sc., F.I.C., Finsbury Technical College, London.

Ozone and Hydrogen Peroxide: their Properties, Technical Production and Applications. By H. VINCENT A. BRISCOE, D.Sc., A.R.C.S., Imperial College of Science and Technology, South Kensington.

The Natural Organic Colouring Matters. By A. G. PERKIN, F.R.S., The Dyeing Department, The University, Leeds; and A. E. EVEREST, D.Sc., PH.D., Technical College, Huddersfield.

Industrial Applications of the Rarer Metals. By WILLIAM G. WAGNER and W. E. F. POWNEY, A.I.C.

Liquid Fuel for Internal Combustion Engines. By Sir BOVERTON REDWOOD, Bart., D.Sc., F.R.S.E., and J. S. S. BRAME, Royal Naval College, Greenwich.

Cellulose-Silk. By C. F. CROSS, B.Sc., F.R.S., F.I.C.

The Zinc Industry. By ERNEST A. SMITH, The Assay Office, Sheffield.

The Electric Arc in Chemical Industry. By J. N. PRING, D.Sc., The University, Manchester.

By-Product Coking Practice. By ERNEST BURY, M.Sc.

Organic Synthetic Reactions: their Application to Chemical Industry. By JULIUS B. COHEN, B.Sc., Ph.D., F.R.S.

Colour in Relation to Chemical Constitution. By E. R. WATSON, M.A., D.Sc., The University, Leeds.

Synthetic Colouring Matters: Triphenylmethane Dyes. By R. ROBINSON, D.Sc., Professor of Organic Chemistry in the University of Liverpool.

Synthetic Colouring Matters: Anthracene and Allied Dye-stuffs. By F. W. ATACK, M.Sc. Tech., B.Sc. (Lond.), F.I.C. of the Municipal School of Technology, Manchester.

Synthetic Colouring Matters: Acridine and Xanthene Dye-stuffs. By JOHN T. HEWITT, M.A., D.Sc., F.R.S., University of London (East London College).

Synthetic Colouring Matters: Azine and Oxazine Dye-stuffs. By JOHN T. HEWITT, M.A., D.Sc., F.R.S., University of London (East London College).

Synthetic Drugs: Local Anæsthetics. By W. H. HURTLEY, D.Sc., St. Bartholomew's Hospital; and M. A. WHITELEY, D.Sc., Imperial College of Science and Technology, South Kensington.

MONOGRAPHS ON INDUSTRIAL CHEMISTRY

EDITED BY SIR EDWARD THORPE, C.B., LL.D., F.R.S.

EDIBLE OILS AND FATS

EDIBLE OILS & FATS

BY

C. AINSWORTH MITCHELL, B.A., F.I.C.

WITH ILLUSTRATIONS

LONGMANS, GREEN AND CO.
39 PATERNOSTER ROW, LONDON
FOURTH AVENUE & 30TH STREET, NEW YORK
BOMBAY, CALCUTTA, AND MADRAS
1918

PREFACE

In this book I have endeavoured to give a concise outline of the chemical composition and properties of the more important oils and fats, together with a description of the methods of extracting them from the crude materials, and of purifying and preparing them for food purposes. A chapter dealing with the physical and chemical methods of examining edible oils is also included, and tables of typical so-called "constants" are given with the descriptions of the individual fats, with the object of enabling any one who has no specialised knowledge of the subject to understand the technicalities of an analysis. With this end in view, the principles rather than the working details of well-known analytical methods have been described.

At the same time, in the hope that this small book may also be of use to the expert, I have given fuller descriptions of more recent methods, and particularly of those which have not yet found their way into the general text-books on the analysis of oils and fats. The mode of arranging the references has also been chosen with the idea of making the book a convenient source of reference. Thus, in the text, in what may be termed the historical references I have cited the original journals, whilst for details or modifications of methods I have given references to the abstracts in English journals, such as the *Analyst* and *Journal of the Society of Chemical Industry*, which are to be found in most laboratories. In the case of the bibliography, which has been made as

full as possible, and therefore includes many references not mentioned in the text, both the original communications and English abstracts of them are usually given.

In connection with the chapter upon the extraction of oils, I wish to acknowledge my indebtedness to Messrs. Rose, Downs and Thomson, of Hull, who have kindly lent the blocks illustrating their most recent machinery.

I also wish to thank the Planters' Margarine Company, of Godley, for details of the most modern types of machinery used in the manufacture of margarine.

C. AINSWORTH MITCHELL.

White Cottage,
The Common,
Amersham.

ERRATUM

p. 61, for *Aleurites moluccana* read *A. triloba.*

CONTENTS

LIST OF ILLUSTRATIONS

EDIBLE OILS AND FATS

CHAPTER I

THE NATURE, PROPERTIES AND COMPOSITION OF FATS

THE word "oil," as used colloquially, is applied to many liquids which often have nothing in common except a certain superficial resemblance. Thus we speak of *oil of vitriol*, *petroleum oil*, *oil of turpentine*, and *linseed oil*, all of which belong to different groups of chemical compounds, and differ widely in their physical and chemical properties. In some cases the name has survived from the days of the alchemists, who regarded oil as one of the five principles of all natural things; and other liquids which resembled these, or were obtained in a similar manner, were afterwards grouped under the same heading.

The class of oils dealt with in this book includes only those fatty compounds which are suitable for human food, whilst similar oils containing a medicinal principle, or essential oils used for flavouring purposes, are only touched upon incidentally.

Essentially there is no fundamental difference between a fat and a fatty oil. An oil which is fluid at the ordinary temperature becomes a fat when chilled, whilst a fat is converted into an oil when heated to a sufficiently high temperature. Arachis oil, for example, which is fluid in summer, solidifies to a consistent fat in winter; and in the case of olive oil, products which will solidify readily are sold under the name of "summer oils."

It is probable that the fats and oils first prepared by man were of animal origin, since these can be separated from the

tissues much more readily than most vegetable fats. Such animal fats would include the tallows, dripping and lard rendered by primitive methods from wild or domestic animals, whilst at a later period butters were made from the milk of the cow, goat, buffalo, etc.

In arctic regions oil separated from the blubber of the whale or seal, or from sea birds, would take the place of the animal fats used in warmer districts, whilst on the coasts of countries such as Japan, where fishing was the staple industry, the separation of fish oils must date back to a very early period.

With regard to the vegetable products, the oil obtained from the olive by hand-pressure appears to have been known in the countries of Southern Europe at the earliest period of which we have any historical record. Subsequently primitive forms of presses were devised for the extraction. In like manner, the oils and fats which could be separated from fruit pulps without elaborate apparatus have been known for centuries to the natives of the countries where they were produced. Palm oil, for example, was separated by the simple expedient of leaving the fruit to decompose in holes in the ground and skimming off the fat as it rose to the surface. Treatment of the material with boiling water marked a further advance in the primitive methods of separating oils from fruits and vegetable seeds. (*See* Chapter III.)

With the invention of simple presses, such as wooden planks weighted with stones, and the introduction of methods for the preliminary roasting of nuts and beans, many other kinds of oils and fats were made available for the use of man.

All nuts and seeds contain a certain proportion of oil, although the quantity is not always sufficient for economical extraction; nor is the oil always suitable for human food. In many instances the seeds also contain poisonous ingredients or substances with a bitter taste, and these become mixed with the extracted oil, which can only be used for food after a special process of purification.

For example, oil from the kernels of the stones of cherries

and similar fruits contains hydrocyanic acid, whilst croton, castor, and curcas oils contain purgative principles, and the mustard-seed oils have a sharp acrid taste due to the presence of the essential oil of mustard.

Properties of Fats

Fats and fatty oils differ from essential oils in being what are known as "fixed compounds." In other words, unlike most essential oils, which can be distilled with little decomposition, or none at all, the fats cannot be volatilised without decomposition, under the ordinary atmospheric conditions, but when heated undergo a process of destructive distillation. They all contain carbon, hydrogen and oxygen, and are for the most part composed of compounds of glycerin or other alcohol with various members of certain groups of acids, which, from their origin, are commonly known as *fatty acids.* When "saponified" by treatment with a solution of an alkali they are decomposed, with the formation of the alkali salts of the fatty acids present, and the liberation of the glycerin or other alcohol in the free condition.

For example, the saponification of tallow by means of potassium hydroxide yields the potassium salts of stearic, palmitic, oleic and linolic acids with free glycerin, whilst beeswax yields chiefly potassium palmitate and free myricyl alcohol.

Fats are readily soluble in many organic solvents such as ether and chloroform, whilst some with a special composition (*e.g.* castor oil) will also dissolve easily in alcohol. Strong acetic acid dissolves different proportions of the various fats and oils, and tests for distinguishing between individual fats have been based upon these differences.

Chemical Composition of Fats

The majority of the fatty compounds are composed of the *glycerides,* or compound ethers of glycerin mentioned above, whilst the corresponding compounds of fatty acids with other alcohols are regarded as *waxes,* from the chemical point of

view, whatever their physical character may be. For example, Japan wax, which consists in the main of the glyceride of palmitic acid, or palmitin, is, chemically considered, not a wax at all, whereas sperm oil, which consists of various alcohols other than glycerin combined with liquid fatty acids, is, strictly speaking, a liquid wax.

Glycerin is capable of combining with one, two, or three acid radicles to form *mono-*, *di-*, or *tri-glycerides*, most of which have been synthetically prepared. Thus, in the case of stearic acid, we can have *monostearin*, $C_3H_5\begin{cases} O St. \\ OH \\ OH \end{cases}$; *distearin*, $C_3H_5\begin{cases} O St. \\ O St. \\ OH \end{cases}$; and *tristearin*, $C_3H_5\begin{cases} O St. \\ O St. \\ O St. \end{cases}$, where *St.* represents the radicle of stearic acid.

Compounds of these various types are known to exist normally in natural fats, the mono- and di-glycerides probably being formed by the gradual hydrolysis of the triglycerides. For example, old rape-seed oil has been shown to contain the diglyceride *dierucin*, which had probably been produced by the hydrolysis of the *trierucin* in the fresh oil.[1]

In the hydrolysis effected by saponification there is evidence that di- and mono-glycerides are formed as intermediate stages in the process. This was shown by Geitel[2] to be probable on physical grounds, and his conclusions were confirmed by Lewkowitsch,[3] who found that the products separated during the fractional saponification of fats had at first increased acetyl values (*q.v.*) as compared with the original fats, but that afterwards the acetyl values fell again. He pointed out that these stages could take place simultaneously, a molecule of triglyceride being converted into diglyceride, while another molecule of monoglyceride was being transformed into free fatty acids and glycerin, and so on. Any deductions drawn from variations in the acetyl values are therefore based on the mean values of the three stages of the hydrolysis at given intervals.

[1] Reimer and Will, *Ber.*, 1886, xix, 3320.
[2] *J. prakt. Chem.*, 1897, 429; 1898, 113.
[3] *Ber.*, 1900, xxxii, 89.

Pure Triglycerides.—Among the principal triglycerides which are likely to be met with in many animal and vegetable fats are the following compounds, which, when synthetically prepared in the pure condition, have the following melting points—

		Melting Point, °C.
Butyrin,	$C_3H_5(O.C_4H_7O)_3$, liquid at ordinary temperatures.	
Laurin,	$C_3H_5(O.C_{12}H_{23}O)_3$	45
Myristin,	$C_3H_5(O.C_{14}H_{27}O)_3$	55
Palmitin,	$C_3H_5(O.C_{16}H_{31}O)_3$	62
Stearin,	$C_3H_5(O.C_{18}H_{35}O)_3$	71·5
Olein,	$C_3H_5(O.C_{18}H_{33}O)_3$, solid at − 6° C.	

Mixed Glycerides.—At one time it was believed that mixed glycerides did not occur in natural fats. That is to say that there could be tristearin, $C_3H_5\begin{cases}OSt\\OSt\\OSt\end{cases}$; tripalmitin, $C_3H_5\begin{cases}OP\\OP\\OP\end{cases}$; or triolein, $C_3H_5\begin{cases}OOl\\OOl\\OOl\end{cases}$, but not a mixed compound containing, for example, two stearic radicles and one oleic radicle, or all three separate radicles, $C_3H_5\begin{cases}OSt\\OP\\OOl\end{cases}$. This conclusion was mainly based on the fact that when an oil such as olive oil was chilled the solid deposit which separated yielded only palmitic acid when saponified, whilst the liquid portion consisted mainly of olein.

There is now, however, ample evidence of the existence of such mixed glycerides in natural fats. Blyth and Robertson[1] pointed out that in the case of cow's butter it was not possible to separate tributyrin from the fat by treatment with alcohol, whereas artificial mixtures of butyrin with other triglycerides could easily be separated in this way. They therefore concluded that a mixed glyceride was present in the fat. The

[1] *Proc. Chem. Soc.*, 1889, 5.

first chemist to separate and definitely identify a mixed glyceride, however, was Heise,[1] who isolated oleo-distearin from the fat extracted from the seeds of the tallow tree, (*Stearodendron stuhlmanni*), and his work was afterwards confirmed by Henriques and Künne.[2]

The insoluble bromides separated by Hehner and Mitchell[3] from linseed oil and marine animal oils agreed in their elementary composition with the bromides of mixed glycerides, and analogous chlor-iodo compounds were isolated by Henriques and Künne (*loc. cit.*) from linseed oil and from butter fat.

The mixed glycerides of palmitic and stearic acids have been isolated from beef and mutton fats and from lard. By repeated recrystallisation of lard from ether, Bömer[4] was unable to separate tristearin from the fat, and in this respect lard appears to differ from beef and mutton fats from which tristearin can be separated. The most insoluble glyceride found in lard was about 3 per cent. of a palmito-distearin, which differed in its melting points (68·5° C. and 51·5° C.), and its crystalline form from the palmito-distearin of mutton fat. Apparently the compound in lard is α-palmito-distearin, whereas the mutton fat glyceride is β-palmito-distearin. About 2 per cent of stearo-dipalmitin was also separated from lard.

The presence of these distinctive glycerides explains the differences in the forms of the crystals deposited from solutions of pure lard and of beef fat in ether (p. 81). Bömer and Limprich[5] prepared β-palmito-distearin synthetically by heating α-distearin under pressure with palmitic acid, and this compound melted at about 63° C., and crystallised from ether in the same form as the palmito-distearin from mutton fat.

Polenske's method of detecting beef and mutton fat in lard by the difference between the melting and solidification points of the fats (p. 82) also depends upon the presence of different mixed glycerides in the fats.

1 *Arb. Kaiserl. Gesundheitsamt*, 1896, 540.
2 *Ber.*, 1899, xxxii, 387. 3 *Analyst*, 1898, xxiii, 317.
4 *Zeitsch. Nahr Genussm.*, 1913, xxv, 321. 5 *Ibid.*, 354.

RANCIDITY OF FATS

When fats are exposed to light and air they gradually undergo a form of decomposition in which products of unpleasant odour and taste are formed. In this change, which is termed "rancidity," a large amount of free fatty acids is often liberated, although, as Ballantyne[1] showed, the rancidity of a fat does not stand in any relationship to the amount of free fatty acids.

Although light promotes the formation of rancidity it is not essential to the process, which appears to be essentially of an oxidising character.

The course of the oxidation was studied by Spaeth,[2] who found that the unsaturated fatty acids were first attacked, and that subsequently hydroxy acids and aldehydes were produced. The fatty acids were liberated, and the proportion of volatile acids in the fat was greatly increased.

According to the observations of Scala[3] the compounds to which rancid fats owe their characteristic odour and flavour are partly of an acid and partly of an aldehyde character, the latter class being volatile. A sample of rancid olive oil yielded on distillation with a current of steam compounds which, when oxidised with potassium permanganate, formed acids including œnanthylic, pelargonic and butyric acids, with smaller amounts of caprylic and caproic and, probably, capric acids.

The rancid odour and taste were attributed to œnanthylic and pelargonic aldehydes, and, to a less extent, to caproic and butyric aldehydes.

Experiments made by various chemists have shown that rancidity is not primarily due to the action of bacteria and mould-fungi, although, as Mjoen[4] proved, once the decomposition has started, the presence of micro-organisms may influence the character of the chemical changes.

[1] *J. Soc. Chem. Ind.*, 1891, x, 29.
[2] *Zeitsch. anal. Chem.*, 1896, xxxv, 471.
[3] *Gazz. Chim. Ital.*, 1908, xxxviii, 307.
[4] *Forschungs Ber.*, 1897, iv, 195.

There is little doubt but that the presence of lipoclastic enzymes in vegetable seeds plays some part in the development of rancidity, since they effect the hydrolysis of the glycerides, and cause a rapid increase in the acid value of such fats as palm oil.

It would appear that in certain stages of rancidity some polymerisation of glycerides must take place, for Brown[1] has noticed the formation of compounds showing the phenomenon of a double melting point (*see* p. 37).

According to Nagel[2] the following classes of compounds may occur in rancid fats. Free fatty acids, hydroxy acids, lactones, alcohols, esters of various fatty acids with higher alcohols, aldehydes, acetals and terpenes. He has based a method purifying rancid fats upon the successive elimination of these different classes of compounds.

Exposure of sesamé oil to light and air produces distinctive oxidation compounds, which, when the oil is shaken with hydrochloric acid, impart a green coloration to the acid layer. This reaction, which is due to Bishop,[3] is not given by fresh sesamé oil. On this fact Kreis[4] has based a test for the presence of rancidity in other fats, fresh sesamé oil being used as the reagent. If, for example, lard which has begun to turn rancid is mixed with fresh sesamé oil and shaken with hydrochloric acid, the acid layer is at once coloured green.

Estimation of the Degree of Rancidity.—A method of estimating the extent to which a fat has become rancid has been based by Issoglio[5] on the proportion of aldehydes, etc., liberated from the fat on distillation with steam under constant conditions, and their measurement by titration with potassium permanganate solution. The weighed quantity of the fat is mixed with water and distilled in a current of steam so that a definite quantity of distillate is collected in ten minutes. An aliquot part of the distillate is then diluted with water,

[1] *J. Amer. Chem. Soc.*, 1899, xxi, 975.
[2] *Amer. Chem. J.*, 1900, xxiii, 173.
[3] *J. Soc. Chem. Ind.*, 1890, ix, 112.
[4] *Chem. Zeit.*, 1899, xxiii, 802.
[5] *Annali Chim. Applicata*, 1916, vi, 1; *Analyst*, 1916, xli, 304.

acidified with sulphuric acid, and boiled for five minutes with a measured quantity of N/100 potassium permanganate solution. After cooling, the liquid is treated with N/100 oxalic acid solution and titrated with permanganate solution.

If N represents the amount of permanganate required for the oxidation, *n* that consumed in a blank test, and P the weight of fat taken, the *oxidisability value* of the fat may be expressed by the equation—

$$X = \frac{(N - n)\,80}{P}$$

Hence the *oxidisability value* represents the number of mgrms. of oxygen required to oxidise the organic compounds separated under constant conditions from the fat.

Issoglio found that the value varied from 3 to 10 in the case of fresh, sound fats, whereas rancid fats gave much higher values.

His experiments bore out the conclusion of Ballantyne (*supra*), that the acid value does not stand in any definite relation to the degree of rancidity. For example, fifteen samples of fresh olive oils of different origin showed acid values ranging from 1·88 to 8·59, and oxidisability values of 3·20 to 10·45; whilst six samples of rancid olive oil showed acid values of 6·51 to 18·56, and oxidisability values of 14·62 to 59·10. When the oxidisability value exceeds 15, it may usually be inferred that the fat has undergone some change such as is produced by rancidity.

CHAPTER II

CONSTITUENTS OF OILS AND FATS

A.—FATTY ACIDS

THE fatty acids obtained from the glycerides of natural fats by hydrolysis or saponification may be classified into two main groups: I. SATURATED, and II. UNSATURATED FATTY ACIDS. The first group comprises the *Acetic* or *Stearic* acid series, whilst the second group includes: (*a*) the *Acrylic* or *Oleic* acid series, (*b*) the *Linolic* acid series, (*c*) the *Linolenic* acid series, and (*d*) *Fatty* acids containing eight or more unsaturated bonds in their molecule.

To these may be added hydroxy-acids such as the ricinoleic acid of castor oil and the acids formed in the oxidation of unsaturated fatty acids.

I.—SATURATED FATTY ACIDS

Acetic Acid Series

These have the general formula, $C_nH_{2n}O_2$, and are typified by acetic acid, one of the best known of the series. In the table on page 11 are included the principal members of this group, together with their formulæ and some of their physical characters.

The lower members of this series are liquids at the ordinary temperature, whilst the remainder are white crystalline solids. Their difference in solubility in water forms the basis of Hehner's method of distinguishing between certain fats, the amount of insoluble fatty acids yielded by a fat being known as the *Hehner value*. The solubility decreases with the rise in the molecular weight of the acids, so that while butyric

acid is readily soluble in cold water, caprylic acid is only sparingly soluble in boiling water, and lauric acid is nearly insoluble therein.

	Formula.	Mol. Weight.	Melting Point.	Boiling Point.	Specific Gravity.	Source.
			° C.	° C. at 760 mm.		
Acetic acid	CH_3COOH	60	—	118	1·0	Acetic fermention
Butyric acid	C_3H_7COOH	88	− 6·5	163·5	0·9781 at 0° C.	Cow's butter
Caproic acid	$C_5H_{11}COOH$	116	− 20·0	205	0·945 at 0° C.	Cow's butter; coconut oil
Caprylic acid	$C_7H_{15}COOH$	144	16·5	237	0·927 at 0° C.	Coconut oil; butter
Capric acid	$C_9H_{19}COOH$	172	31·3	270	0·930 at 37° C.	Coconut oil; butter
Lauric acid	$C_{11}H_{23}COOH$	200	43·5	176 (15 mm.)	0·875 at 43·5° C.	Coconut oil; palm-kernel oil
Myristic acid	$C_{13}H_{27}COOH$	228	53·8	200·5 (15 mm.)	0·862 at 53·6° C.	Coconut oil, nutmeg butter
Palmitic acid	$C_{15}H_{31}COOH$	256	62·6	215 (15 mm.)	0·853 at 62·6° C.	Palm-kernel oil, Japan wax, lard, butter, etc.
Stearic acid	$C_{17}H_{35}COOH$	284	69·3	232 (15 mm.)	0·845 at 69·3° C.	Most animal fats and many vegetable fats
Arachidic acid	$C_{19}H_{39}COOH$	312	77·0	—	—	Arachis oil
Behenic acid	$C_{21}H_{43}COOH$	340	80 to 82	—	—	Oil of ben, black mustard-seed oil
Lignoceric acid	$C_{23}H_{47}COOH$	368	80·5	—	—	Arachis oil, etc.
Carnaubic acid	$C_{23}H_{47}COOH$	368	72·5	—	—	Carnaubic wax, wool fat
Cerotic acid	$C_{25}H_{51}COOH$	396	78·0	—	—	Beeswax, carnauba wax, wool fat
Melissic acid	$C_{29}H_{59}COOH$	452	88·5	—	—	Beeswax

The more soluble acids are also readily volatile in a current of steam, and on this property is based the *Reichert value* of fats (*q.v.*). The volatility, like the solubility, decreases as the molecular weight of the fatty acids rises, so that lauric acid is barely volatile, and the members of the series next above it are practically non-volatile, without decomposition, at the ordinary atmospheric pressure. It is possible, however, to distil them, with but little change, in a vacuum or under reduced pressure.

The melting-points of mixtures of the higher fatty acids

are lower than the individual melting-points of either of the constituents of the mixture, and this has led, in some instances, to such mixtures being regarded as individual fatty acids.

The fatty acids, with an uneven number of carbon atoms in their molecule, of which margaric acid, $C_{17}H_{32}O_2$, may be taken as typical, have been prepared synthetically; but some, at least, of the instances where they have been alleged to be present in natural fats, stand in need of confirmation. For example, Nordlinger[1] claimed to have isolated a fatty acid, isomeric with margaric acid from palm oil, and gave it the name of *daturic acid;* whilst Holde and Stange[2] isolated from olive oil a mixed glyceride which they regarded as oleo-dimargarin.

A determination of the melting point of a mixture of two fatty acids affords a means of approximately estimating the proportion of each constituent (p. 37).

Butyric Acid, which is present as a glyceride in butter, is a liquid with a characteristic unpleasant odour. It is readily soluble in water, as is also the case with many of its salts. Calcium butyrate, however, has the property of being more soluble in cold than in hot water.

Caproic Acid, $C_6H_{12}O_2$, is present as a glyceride in several fats, notably butter fat, coconut oil and palm oil. It is less soluble than butyric acid in water. It is distinguishable from butyric acid by forming an insoluble zinc salt.

Caprylic Acid, $C_8H_{16}O_2$, occurs as a glyceride in milk fats and in coconut and palm oils. It melts at 16·5° C. to a clear liquid, which, when chilled to 12° C., solidifies in laminated crystals. Its specific gravity at 0° C. is 0·9270.

Capric Acid, $C_{10}H_{20}O_2$, is present as a glyceride in the butter fat of various animals and in vegetable fats of the type of coconut oil. It forms fine pointed crystals which melt at 31·3° C. It is only very sparingly soluble in cold water, and even boiling water dissolves only 0·1 per cent. of the acid.

Lauric Acid, $C_{12}H_{24}O_2$, is present as the glyceride laurin

[1] *Ber.,* 1892, xxv, 578.

[2] *Ibid.,* 1900, xxiv, 2402.

in many vegetable fats, including laurel oil and coconut oil, and is also a constituent of spermaceti. When distilled at the ordinary pressure it undergoes some decomposition, but can be distilled in a current of steam. On this fact is based Polenske's method of estimating coconut oil in butter.

It is only very slightly soluble in boiling water. The magnesium salt is practically insoluble in water (0·04 per cent. at 100° C.), but dissolves to some considerable extent in hot alcohol (12·6 per cent.).

Myristic Acid, $C_{12}H_{28}O_2$, is present as the glyceride, myristin, in nutmeg butter, coconut oil, and many other vegetable fats, and also occurs in lard, butter fat and other animal fats.

It crystallises in plates, melting at 53·8° C. It is the first acid in the ascending series which is quite insoluble in water, and it is only volatile to a slight extent in a current of steam. The barium salt dissolves to a very small extent in water and in alcohol.

Palmitic Acid, $C_{16}H_{32}O_2$, is present in the form of glycerides in most animal and vegetable fats, and is a principal constituent of palm oil and Japan wax.

When pure it crystallises from alcohol in fine bunches of needles, melting at 62·6 C., and having a specific gravity of 0·8412 at 80·4° C. It is much more soluble than stearic acid in cold alcohol, and advantage is taken of this fact in Hehner and Mitchell's method of estimating stearic acid (p. 52). The salts of palmitic acid are also somewhat more soluble than the corresponding stearates, which they otherwise closely resemble.

Stearic Acid, $C_{18}H_{36}O_2$, is present as a glyceride in many animal and vegetable fats, notably in beef fat and cacao butter. It is much less soluble than palmitic acid in alcohol.

Magnesium stearate is soluble in hot alcohol, but separates out as a crystalline deposit on cooling the solution. The potassium and sodium salts undergo hydrolytic dissociation in aqueous solution, and hence it is necessary to add glycerin or alcohol when titrating fatty acids with aqueous solutions of alkalis.

Lead stearate is still less soluble than lead palmitate in ether, 100 c.cm. dissolving only 0·015 grm. On the difference between these salts and lead oleate in their behaviour towards ether was based the earliest method of separating solid from liquid fatty acids (p. 51).

Arachidic Acid, $C_{20}H_{40}O_2$, takes its name from arachis oil, in which it is present in considerable quantity. It also occurs in small amounts in butter fat, rape oil, cacao butter and other fats. It crystallises in small flat plates, which melt at 77° C. It is much less soluble than stearic acid in hot alcohol, but is soluble without difficulty in ether and petroleum spirit. The arachidates resemble the corresponding stearates, but are less soluble in various solvents.

Behenic Acid, $C_{22}H_{44}O_2$, is found as a glyceride in oil of ben. It is only sparingly soluble in alcohol, from which it crystallises in needles, melting at 80° to 82° C.

Lignoceric Acid, $C_{24}H_{48}O_2$, is present in arachis oil as a glyceride, and separates from a solution of the mixed fatty acids of that oil in association with the arachidic acid. It has a somewhat higher melting point (80·5° C.), and forms salts which are still less soluble than the corresponding compounds of arachidic acid.

Cerotic Acid, $C_{26}H_{52}O_2$, is a constituent of carnauba wax and beeswax, in which it is present in the free state; and of wool wax, in which it is present in combination with ceryl alcohol. It crystallises from a hot alcoholic solution in fine needles, melting at 78° C. The alkali salts are readily soluble in boiling water, and the magnesium salt in hot alcohol. The lead salt is insoluble in ether, but is dissolved by benzene, from which, on cooling, it separates in needles.

Melissic Acid, $C_{30}H_{60}O_2$, is a constituent of beeswax, in which it occurs in the free condition. It is readily soluble in hot alcohol and petroleum spirit, but is much less soluble in ether. When separated from its solutions it crystallises in fine needles, which melt at 88·5° C. Lead melissate is soluble in boiling chloroform, but is insoluble in alcohol and in ether.

II.—Unsaturated Fatty Acids

In the unsaturated fatty acids the molecule contains one or more pairs of carbon atoms united together by a double bond, which may be found in various positions in the chain, producing isomeric acids with distinct properties. It is possible to saturate this unsaturated bond by means of various elements, including the halogens, oxygen and hydrogen; and the amount of iodine or its equivalent absorbed by an unsaturated fatty acid or glyceride thus affords a measure of its degree of unsaturation (*see* p. 48).

(*a*) *The Acrylic or Oleic Acid Series*

The fatty acids in this series have the general formula $C_nH_{2n-2}O_2$, and are typified by oleic acid, which is the most common fluid fatty acid in oils and fats. They include the following acids—

Fatty Acid.	Formula.	Mol. Weight.	Melting Point.	Boiling Point.	Specific Gravity.	Source.
			°C.			
Tiglic . .	$C_5H_8O_2$	110	64	198·5	0·964	Croton oil
Physetoleic	$C_{16}H_{30}O_2$	254	30			Sperm oil, seal oil
Hypogæic .	$C_{16}H_{30}O_2$	254	34	230 (10 mm.)		Arachis oil
Oleic . .	$C_{18}H_{34}O_2$	282	14	286 (100 mm.)	0·898 (15° C.)	Most fatty oils
Erucic . .	$C_{22}H_{42}O_2$	338	33	256 (10 mm.)		

When the acids of this group are fused with potassium hydroxide they are decomposed, although not quantitatively, with the formation of the potassium salts of two fatty acids of the acetic series and free hydrogen. For example, in the case of oleic acid the reaction is as follows—

$$\underset{\text{Oleic Acid}}{C_{18}H_{34}O_2} + \underset{\text{Potassium Hydroxide}}{2KOH} = \underset{\text{Potassium Palmitate}}{K.C_{16}H_{31}O_2} + \underset{\text{Potassium Acetate}}{K.C_2H_3O_2} + H_2$$

This reaction was at one time utilised on a large scale in

France for the manufacture of solid candle material from oils, but, owing to the danger attending the evolution of large quantities of hydrogen gas, has long since been abandoned.

Moreover, the method of hydrogenating oils in the presence of a catalytic agent has now solved the problem of converting liquid oils into solid fats. (*See* Chap. VIII.)

When oxidised by means of potassium permanganate, the fatty acids of this series are converted into the corresponding dihydroxy acids, although not quantitatively, since other oxidation products are simultaneously produced. The characteristics of the resulting hydroxy compounds afford the means of identifying the nature of the fatty acids in an oil (p. 22).

Tiglic Acid, $C_5H_8O_2$, which is found as a glyceride in croton oil, melts at 64·5° C. and boils at 198·5° C. When fused with potassium hydroxide it yields acetic and propionic acids. Restricted oxidation with potassium permanganate converts it partially into dihydroxytiglic acid, whilst carbon dioxide, acetic acid and acetaldehyde are also produced.

Hypogæic Acid, $C_{16}H_{30},O_2$, has been separated from arachis oil, and is said to have been found in maize oil. The synthetically prepared acid melted at 33° to 34° C. and boiled at 230° under a reduced pressure of 10 mm. Under the influence of nitrous acid vapour hypogæic acid is converted into its stereo-isomeric compound *gaidic acid*, which melts at 39° C. (*See* Elaidin Reaction.)

Physetoleic acid, $C_{16}H_{30}O_2$, is a fatty acid, isomeric with hypogæic acid, from which it differs, however, in not yielding a stereo-isomeric acid in the elaidin reaction. It occurs as a glyceride in seal oil.[1]

Oleic Acid, $C_{18}H_{34}O_2$, which gives its name to this series of unsaturated fatty acids, is a constituent of most oils and fats. It is a colourless oil, which rapidly absorbs oxygen from the air and becomes yellow. It melts at 14° C., and when chilled to 4° solidifies to a crystalline mass.

It is probable that its unsaturated double bond occurs in the middle of the chain, and the following constitutional

[1] Ljubarsky, *J. prakt. Chem.*, 1898, 26.

formulæ have been based on a consideration of the various reactions which it gives—

$$\begin{array}{l} CH_3.(CH_2)_{13}.C \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad HC.CH_2.COOH \, * \end{array}$$

Or—

$$\begin{array}{l} CH_3.(CH_2)_7CH \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad CH.(CH_2)_7COOH \, \dagger \end{array}$$

Oleic acid combines with two atoms of chlorine, bromine or iodine to form addition compounds, as for example—

$$\underset{\text{Oleic acid}}{C_{18}H_{34}O_2} + \underset{\text{Iodine}}{I_2} = \underset{\text{Di-iodo stearic acid}}{C_{18}H_{34}I_2O_2}$$

It can be made to combine with nascent hydrogen by heating it in a sealed tube with fuming hydriodic acid and red phosphorus, the unsaturated bond then becoming saturated and stearic acid being produced. Hydrogenation in presence of a metallic catalyst, however, is a better method of effecting the combination.

The alkali salts of oleic acid are readily soluble in water. The lithium salt dissolves in hot alcohol, but is insoluble in ether and benzene.

Lead Oleate, $Pb(C_{18}H_{33}O_2)$, differs from the lead salts of palmitic and stearic acid in being soluble in ether, and on this property is based a method of separating liquid from solid fatty acids (p. 51). It is a white powder which melts at 80° C.

The barium salt is only slightly soluble in hot benzene.

Elaidic Acid.—By the action of nitrous acid vapour oleic acid is converted into an isomeric compound known as elaidic acid, the constitutional formula of which may be represented as—

$$\begin{array}{r} CH_3.(CH_2.)_{13}CH \\ \| \\ COOH.CH_2.CH \end{array} \quad \text{or} \quad \begin{array}{r} CH_3(CH_2)_7.CH \\ \| \\ COOH(CH_2)_7CH \end{array}$$

* Saytzeff, *Ber.*, 1894, xxvii, Ref. 577.
† Baruch, *ibid.*, 1894, xxvii, 173.

according to whether the formula of Saytzeff or of Baruch (*supra*) is accepted for oleic acid.

Elaidic acid, when purified by recrystallisation from alcohol, melts at 43·5° to 44·5° C.,[1] and has a specific gravity of 0·8505 at 79·4° C. When distilled it undergoes very slight decomposition. When treated with iodine it is transformed into iodo-stearic acid; and this when boiled with alcoholic potassium hydroxide solution is largely reconverted into oleic acid, together with some iso-oleic acid.

Iso-oleic Acid is another solid isomer of oleic acid which Saytzeff[2] prepared by distilling β-hydroxystearic acid under reduced pressure. It is also formed in the distillation of the "stearic acid" of commerce.

It crystallises in plates melting at 44° to 45° C., and has been assigned the following constitutional formula—

$$\begin{array}{l} CH_3(CH_2)_{14}.CH \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad H.C.\ COOH. \end{array}$$

The dihydroxystearic acid which it yields on oxidation with potassium permanganate is not identical with that given by oleic acid (p. 22).

(*b*) *The Linolic Acid Series*

These acids have the general formula $C_nH_{2n-4}O_2$, and are thus more unsaturated than the members of the oleic acid series. A few of them occur naturally in oils, whilst others have been prepared from corresponding acids in the oleic acid series by treating the bromination product with alcoholic potassium hydroxide so as to remove both hydrogen and bromine together. For example, oleic acid combines with bromine to form dibromstearic acid, and the latter, after removal of two atoms of hydrogen and bromine as hydrobromic acid, yields *stearolic acid*, which is isomeric with linolic acid—

$$C_{18}H_{34}Br_2O_2 - 2HBr = C_{18}H_{32}O_2.$$

The fatty acids of this series combine with four atoms of

[1] Farnsteiner, *Zeitsch. Nahr. Genussm.*, 1899, ii, 5.
[2] M. and A. Saytzeff, *J. prakt. Chem.*, 1898, lvii, 27.

a halogen to form tetrabromides as, for example, in the case of linolic acid—

$$\underset{\text{Linolic Acid + Bromine}}{C_{18}H_{32}O_2 + Br_4} = \underset{\text{Tetrabromstearic Acid}}{C_{18}H_{32}Br_4O_2};$$

and from the resulting compounds the halogen may be removed again by the action of nascent hydrogen or other reducing agents. When oxidised with alkaline potassium permanganate acids of the linolic series yield, as their main derivatives, tetrahydroxy compounds, with smaller quantities of other oxidation products.

The principal acids of this series yet studied are the following—

Fatty Acids.	Formula.	Mol. Weight.	Melting Point.	Boiling Point.	Sources.
			° C.		
Palmitolic	$C_{16}H_{28}O_2$	252	42	—	From hypogæic acid
Elæomargaric . .	$C_{17}H_{30}O_2$	266	48	—	Tung oil
Elæostearic	$C_{17}H_{30}O_2$	266	71	—	Japanese wood (tung) oil
Stearolic .	$C_{18}H_{32}O_2$	280	48	—	
Linolic . .	$C_{18}H_{32}O_2$	280	Fluid	290° (89 mm.)	Maize oil, cotton-seed oil, and in most oils
Tariric . .	$C_{18}H_{32}O_2$	280	50·5	—	Tariri seed
Benolic . .	$C_{22}H_{40}O_2$	336	57·5	—	From erucic acid

Palmitolic, stearolic and benolic acids have been prepared by means of the bromine reaction (p. 18) from corresponding acids of the oleic series, and have not yet been discovered in natural fats and oils.

Elæostearic or *elæomargaric Acid*, $C_{17}H_{30}O_2$, occurs as a glyceride in tung oil. The fatty acid, separated by Cloez,[1] was termed elæomargaric acid. It melted at 48° C., but an isomeric acid melting at 71° C. has been isolated from the same oil.

Linolic Acid, $C_{18}H_{32}O_2$, is present as a glyceride in most fats, and may be obtained in quantity from semi-drying oils, such as maize and cotton-seed oils. An acid prepared by Norton and Richardson from linseed oil had a specific gravity of 0·9108 at 15°/4° C.

[1] *Compt. rend.*, 1875, lxxxi, 469.

It combines with bromine to form linolic tetrabromide, $C_{18}H_{32}O_2Br_4$, melting at 114° to 115° C., and from this the bromine can again be removed by reduction with zinc and hydrochloric acid, regenerating the original linolic acid.

When oxidised with alkaline permanganate solution linolic acid yields a tetrahydroxystearic acid, $C_{17}H_{31}(OH)_4COOH$, which is known as *sativic acid*, melting at 173° to 174° C., together with some other oxidation products, such as azelaic acid.

The isomeric stearolic acid, prepared as described above, melts at 48° C. The following structural formula is suggested by Baruch[1] as representing its constitution—

$$C_8H_{17}.C{:}C.[CH_2].COOH.$$

Tariric Acid, $C_{18}H_{32}O_2$, is another fatty acid isomeric with linolic acid. It is contained as a glyceride in the seeds of a South American shrub. The fatty acid is solid at the ordinary temperature (melting point 50·5° C.), whilst its tetrabromide melts at 125° C.

Chaulmoogric Acid, $C_{18}H_{32}O_2$, which has the same elementary composition as linolic acid, may be mentioned here, although it only absorbs two atoms of halogens instead of four, and when oxidised yields a dihydroxy instead of a tetrahydroxy acid. It was found by Power and Gornall in the oil from chaulmoogra seeds.[2]

(*c*) *Linolenic Acid Series*

The presence of acids still more unsaturated than linolic acid was inferred by Hazura and Grüssner from the composition of the products obtained on oxidising the liquid fatty acids of linseed, hemp and walnut oils by means of alkaline permanganate solution; and their conclusion has since been confirmed by other workers.

Linolenic Acid, $C_{18}H_{30}O_2$, is present as a glyceride in linseed and other drying oils, and to a less extent in rape oil. On treating a solution of the mixed fatty acids of linseed oil in ether or acetic acid with bromine an insoluble

[1] *Ber.*, 1894, xxvii, 172. [2] *J. Chem. Soc.*, 1904, lxxxv, 835.

bromide is obtained, melting at 180° to 181° C. A specimen prepared by Hehner and Mitchell[1] contained 61·80 per cent. of bromine as against 63·31, the theoretical amount in linolenic hexabromide. When reduced with nascent hydrogen, linolenic hexabromide yields linolenic acid, although the yield is less than 50 per cent. of the theoretical amount on account of the rapid oxidation of the fatty acid as it is liberated.

Linolenic acid is a colourless oily liquid which rapidly turns yellow through oxidation. It has a specific gravity of 0·9228 at 15·5° C. and an iodine absorption approximating to 274·1 (Hazura 245, Hehner and Mitchell 241·8).

When oxidised with potassium permanganate it yields a hexahydroxystearic acid, $C_{17}H_{29}.(OH)_6.COOH$, melting at 203° to 205° C., which Hazura termed linusic acid.

Isolinolenic Acid, which is isomeric with linolenic acid, has not been isolated in the free state, but its existence in linseed oil is inferred from the fact that the mixed fatty acids yield a non-crystalline hexabromide, and that on oxidation with permanganate a hexahydroxy acid, *isolinusic acid* (melting at 173° to 175° C.), is obtained.

Jecoric Acid, $C_{18}H_{30}O_2$, is another isomer of linolenic acid, the existence of which in cod-liver oil was inferred by Fahrion. The fact that the fatty acids of cod-liver oil yielded an insoluble bromide containing 62·91 per cent. of bromine (theory for jecoric acid,[1] 63·31) was cited by Hehner and Mitchell as evidence in support of the existence of this acid. Similar compounds are also obtainable from other fish and marine animal oils.

(*d*) *Acids of the Series* $C_nH_{2n-8}O_2$

Clupanodonic Acid, $C_{18}H_{28}O_2$, was isolated from the fatty acids of Japanese sardine oil by Tsujimoto by reducing an octobromide. It is a liquid with an iodine value of 344 (theory = 368).

Acid, $C_{20}H_{32}O_2$:—A liquid fatty acid with a composition corresponding to the formula $C_{20}H_{32}O_2$ was isolated by Bull[2] from the fatty acids of cod-liver and other fish oils.

[1] *Analyst*, 1898, xxiii, 2, 317.
[2] *Chem. Zeit.*, 1899, xxiii, 996, 1043.

Isanic Acid, $C_{14}H_{20}O_2$, is the name given to a solid fatty acid melting at 41° C., which Hebert[1] isolated from the oil of I'Sano seed.

(*e*) *Hydroxylated Acids*

Ricinoleic Acid, $C_{18}H_{34}O_3$, is found as a glyceride in castor and some other oils. When purified it melts at 16° to 17° C., but cannot be distilled, even under greatly reduced pressure, without undergoing decomposition. When reduced with hydriodic acid and phosphorus it is converted into stearic acid, whilst on oxidation with permanganate it yields trihydroxystearic acid. In the elaidin reaction it yields ricinelaidic acid, melting at 52° to 53° C.

From a consideration of the reactions which it gives the following structural formula has been assigned to ricinoleic acid—

$$CH_3.(CH_2)_5.CH.OH.CH = CH.(CH_2)_8.COOH.$$

Hydroxystearic Acids.—The following table summarises the various saturated hydroxystearic acids, obtained by oxidising the acids described in the preceding pages—

Acids.	Formula.	Melting Point.	Source.
		° C.	
Dihydroxystearic . .	$C_{17}H_{33}(OH)_2COOH$	136·5	Oleic acid
Trihydroxystearic . .	$C_{17}H_{33}(OH)_3COOH$	140 to 142	Ricinoleic acid from castor oil
Tetrahydroxystearic acid (sativic acid)	$C_{17}H_{31}(OH)_4COOH$	173 to 174	Linolic acid
Hexahydroxystearic acid (linusic acid)	$C_{17}H_{29}(OH)_6COOH$	203 to 205	Linolenic acid
Isohexahydroxystearic acid (isolinusic acid)	$C_{17}H_{29}(OH)_6COOH$	173 to 175	Linseed oil and hempseed fatty acids (supposed isolinolenic acid)

B.—ALCOHOLS: GLYCEROL (GLYCERIN)

The alcohol glycerin is the principal constituent, other than fatty acids, of oils and fats, and an outline has already been given of the way in which it combines with fatty acids to form glycerides.

[1] *Bull. Soc. Chim.*, 1896, xv, 941.

It is best known as a thick viscid liquid, but when cooled sufficiently it forms crystals, which melt at 20° C. It has a specific gravity of 1·265 (100 per cent. glycerol) and in the pure condition boils at 290° C.

It mixes in all proportions with water and alcohol, is sparingly soluble in ether, but insoluble in petroleum spirit and chloroform.

When heated with a dehydrating agent, such as hydrogen potassium sulphate, it is decomposed, and yields acrolein, $CH_3 = CH.COH$.

It is readily oxidised by oxidising agents such as potassium bichromate, permanganate, etc.; and on this property is based a standard method of estimating glycerin.

Other Alcohols

Other higher alcohols occur in fats and waxes such as cetyl alcohol $C_{16}H_{34}O$, in combination with palmitic acid in spermaceti, ceryl alcohol, $C_{26}H_{54}O$ in Chinese wax, and myricyl alcohol, $C_{30}H_{62}O$ in beeswax. The esters containing these alcohols are not so readily decomposed as are glycerides, and a much longer time is therefore required for their saponification.

Cholesterol, $C_{27}H_{46}O$, is present in all animal fats, notably cod-liver oil which contains upwards of two per cent. An analogous compound or compounds (*phytosterol*), apparently isomeric with cholesterol, is found in vegetable fats. On the difference in the physical characters of the two compounds is based a trustworthy method of distinguishing between animal and vegetable fats (*see* p. 53).

Sitosterol, $C_{27}H_{44}O + H_2O$, contained in wheat and rye, and *stigmasterol,* which has been prepared from the oil of Calabar beans are constituents or isomeric forms of, phytosterol.

CHAPTER III

EXTRACTION AND PURIFICATION OF OILS AND FATS

Oil Presses.—The primitive forms of presses which were in general use prior to the introduction of steam and hydraulic power are still to be found in various parts of the world. In some of these presses the pulp is wrapped in sacks, and placed between boards which are pressed together by means of wedges driven home by a hammer, or by means of a lever between them and the framework of the press.

Screw presses, in which the pressure was applied by means of a screw turned by the application of long levers worked by hand, were common in factories in the earlier part of last century; but, except in out-of-the-way places, they have long been superseded by steam or hydraulic presses.

A method of mechanical pounding, in which the seeds are crushed in mortars termed "stamps," is still not quite obsolete, though, for the most part, it has been replaced by the use of rollers or "edge runners."

An early type of press, which from its mode of action is known as the "elbow press," is still employed in many places, and particularly in America, for expressing melted fat from animal fatty tissues. By the action of a screw, which may be worked by hand or driven by a band from an engine, the "elbows," in two pairs of vertical levers, are gradually brought together, and the ram forced down into the receiving-box of the press.

A more elaborate form of wedge-press is still in use in Germany. The bags containing the crushed seed are introduced into an iron frame, and loose wooden wedges are driven home by means of heavy beams which are suspended

vertically from a frame above the press, and can be raised or lowered at will by means of a system of ropes. After all the oil has been expressed, other beams are made to fall on the wedges, which are thus released, enabling the bags of expressed oil-cake to be removed from the press.

An apparatus used in some of the oil-works in Marseilles effects the expression by means of a principle similar to that of the wedge-press.[1] It is known as the "Estrayer Cylinder," and consists essentially of two cylinders, one of which is jointed so that it can be forced upwards into the other. The crushed seeds to be expressed are placed in special bags or screens of esparto grass, which, owing to the peculiar construction of the press, will withstand a pressure much greater (500 kilos. per sq. cm.) than can be applied to the bags in an ordinary press, without risk of breaking them. Quantities of 80 to 100 kilos. of seeds can be expressed in about thirty-five minutes.

Modern improvements on the primitive screw-press are sometimes used for the expression of oil from material for which a heavy pressure is not necessary. The top of the plunger is connected with a long screw, which engages concentrically with a horizontal toothed wheel, whereby it is lowered or raised in the pressing-box. This wheel is set in motion by a worm on a horizontal shaft, which is turned by a belt from an engine. The pressing-box is surrounded by a steam casing of wrought iron, so that if required the material can be heated during the expression.

Hydraulic Presses.—In most modern oil factories the expression of oil from seeds and the like is effected by means of hydraulic presses. The bags of material are placed in pressing-boxes, which are fitted one above the other into the press; and the pressure is applied by a ram, which is raised from below by water being admitted into its cylinder, either from an accumulator or through the action of a force-pump. In the latter method the ram is raised in a series of jerks, which gives better results than a steady pressure, for expressing oil from seeds.

[1] *J. Soc. Chem. Ind.*, 1893, xiii, 49.

The sides of the pressing-boxes are perforated with holes through which the expressed oil escapes into channels whence it can be drawn off.

Various modifications of this type of press are in use. Some are made to work horizontally instead of vertically, whilst in others the pressing-boxes are carried on a rotating platform, so that each in turn is brought automatically under the pressure of a ram which is worked by an accumulator.

In other presses, again, means are provided for dispensing with pressing-cloths, the pressing-boxes being constructed with movable sides, which can be fixed so as to retain the oil-cake.

One of the types of press is adapted for expressing seed which has been crushed and heated. The cakes of hot crushed seed coming from a moulding machine are introduced between corrugated plates in the press, and are subjected to a pressure which is gradually increased up to about two tons per square inch. (*See* Fig. 1.)

Oil-cake.—The residual oil-cake left after expression of the oil varies in size from about 14 to 30 ins. in length by about 6 to 10 ins. in width, according to the size of the press, and usually weighs from about 6 to 12 lbs. or more.

When the seed requires a second crushing to remove the oil, as in the case of rape seed, the oil-cake is often reground before the second pressing.

In the production of the finest type of edible oils, such as arachis and sunflower-seed oils, the expression is effected in stages. The crushed seeds are first pressed at a moderate pressure, and the oil thus separated is known as "cold-drawn oil," and fetches the highest price. The residual oil-cake is again crushed, moistened with water and pressed again, whereby a second quality of oil is obtained. Finally, the oil still left in the cake is extracted by regrinding the residue and expressing it while hot, which yields a third grade of oil of much poorer quality than either of the cold-drawn oils.

In the case of certain seeds, such as sesamé seed, the pressing is usually repeated, so as to separate two grades of oils, but oil seeds not intended for food are generally heated and expressed only once. The residues from the final press-

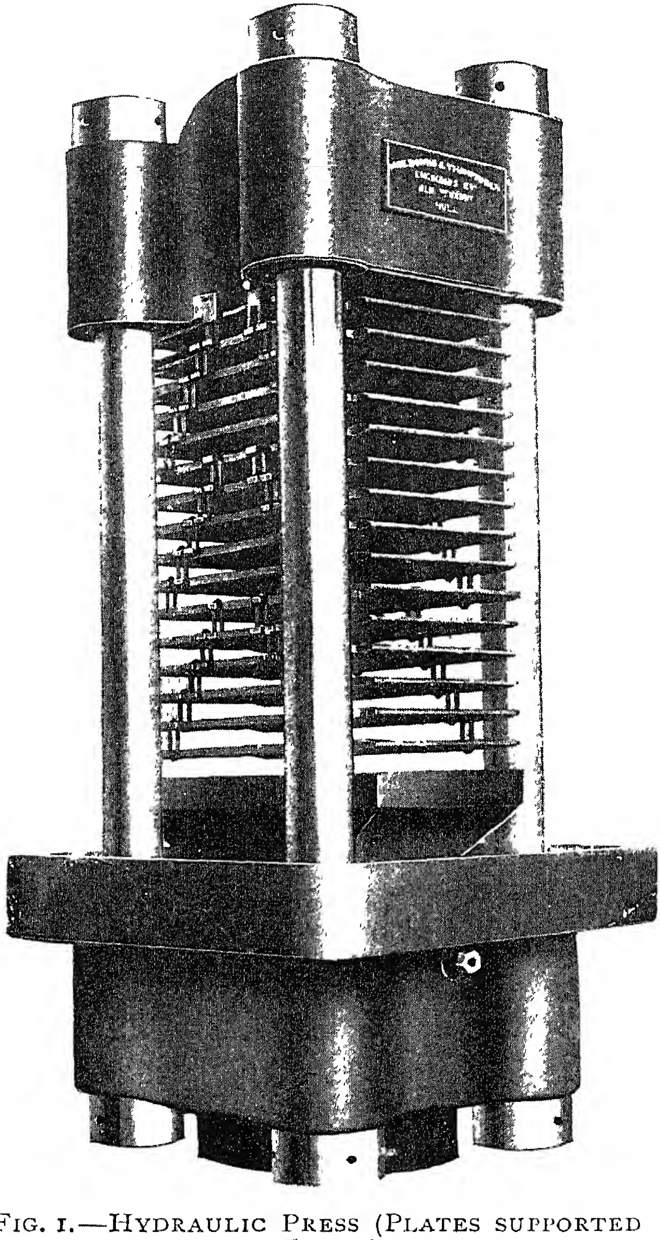


FIG. 1.—HYDRAULIC PRESS (PLATES SUPPORTED BY LINKS).

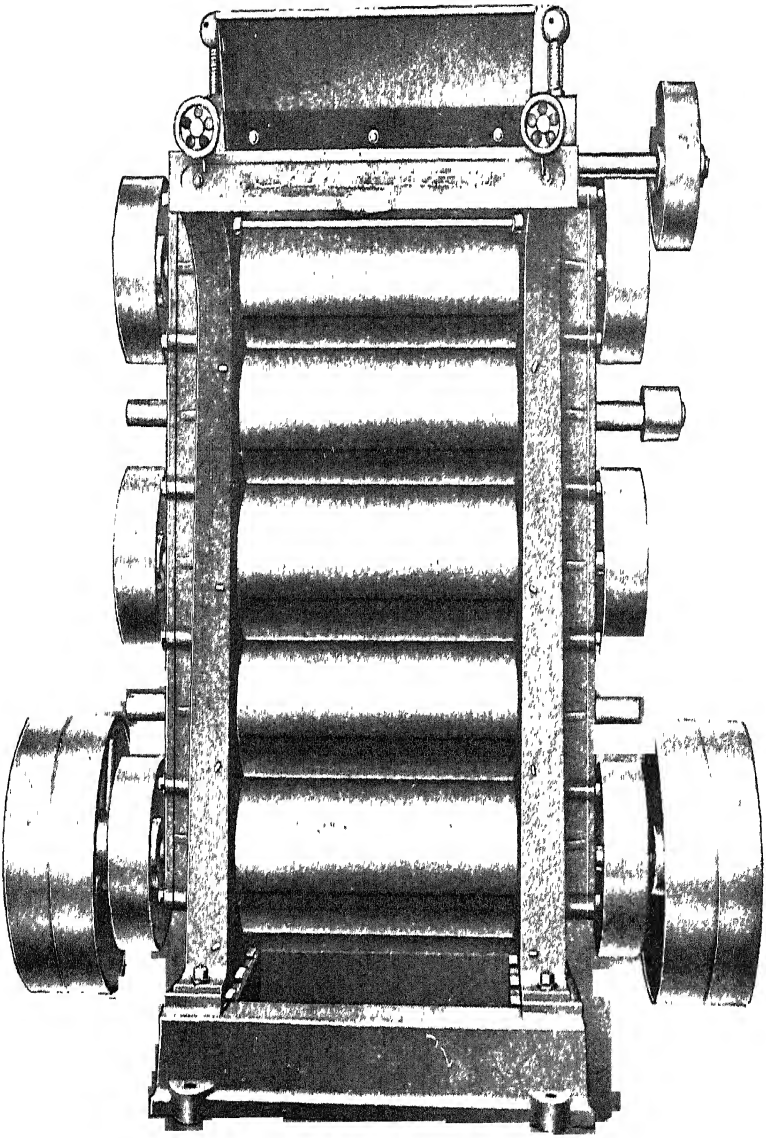


FIG. 2.—CRUSHING ROLLERS (ANGLO-AMERICAN SYSTEM).

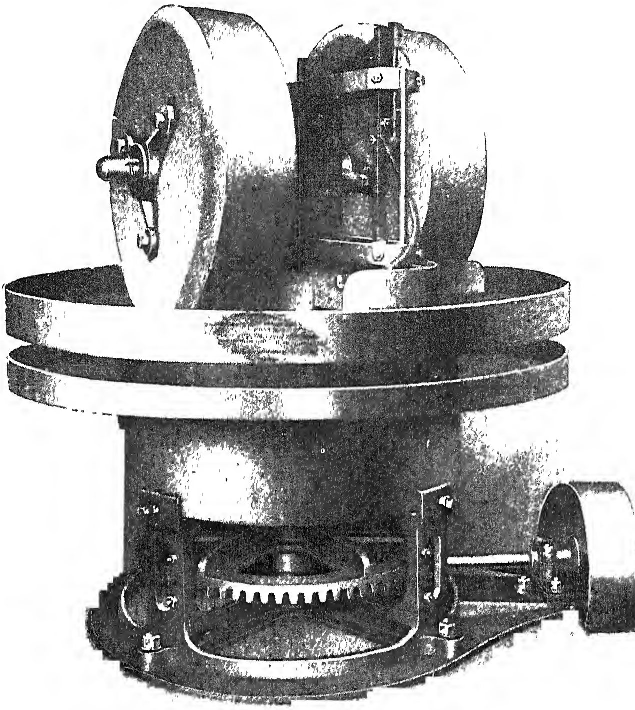


FIG. 3.—ANGLO-AMERICAN EDGE-STONES.

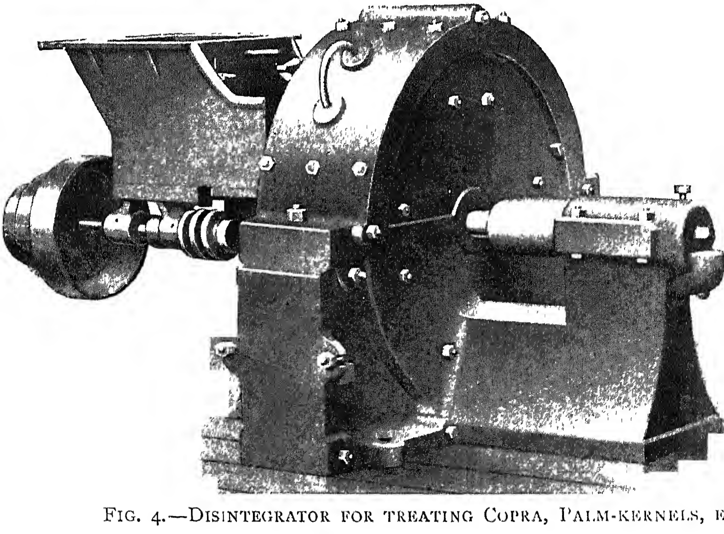


FIG. 4.—DISINTEGRATOR FOR TREATING COPRA, PALM-KERNELS, ETC.

ings often contain sufficient oil to repay the expense of extraction with a solvent.

Oil-cakes vary in composition considerably, both with the nature of the seed and the mode of expression. They usually contain from about 10 to 13 per cent. of water, 8 to 10 per cent. of oil, 2 to 6 per cent. of nitrogen and 6 to 12 per cent. of mineral matter (ash). Owing to exposure of the oil to the air in a fine state of division oxidation takes place rapidly, and the acidity, as free fatty acids, may soon rise from less than 5 to over 20 per cent.

Crushing Rollers.—Few oil-bearing materials are suitable for immediate expression of the oil, and in most cases a preliminary crushing and heating is necessary to rupture the walls of the cells which contain the oil.

The crushing is commonly effected by means of superposed rollers, which are so arranged that the seed passes from a hopper through the uppermost pair of rollers, and is thence successively delivered by means of slanting shoots and guides to the spaces between the third, fourth and fifth rollers. It is thus crushed four times on its way from the top to the bottom of the "rolls," and is more thoroughly broken up than was possible by the older type of single rollers. (*See* Fig. 2.)

Edge-runners.—In the case of some kinds of vegetable-oil material, notably copra and cotton seed, the crushing may be more rapidly effected by means of edge-runners. In these crushing-machines one or two stone rollers with chamfered edges and having a diameter up to 8 ft., are made to turn while revolving in a shallow circular trough, the bed of which is also of stone about 6 ft. in diameter. (*See* Fig. 3.)

Another type of apparatus suitable for the disintegration of material such as copra, palm-kernels and the like, is shown in Fig. 4.

Heating Apparatus.—After being crushed the seeds are heated in a circular steam-jacketed pan known as a "kettle," being meanwhile kept in motion by a revolving agitator driven by a belt.

In the Anglo-American system the kettle is also provided

of a series of plates. When these are packed together in the press their projecting edges meet, so that a space in which is the filter cloth is left between each consecutive plate and its neighbour, and the solid impurities separated from the oil gradually accumulate in these spaces.

Separation of Stearines from Oils

The so-called "stearines" are the more solid portions of oils which deposit when the oil is allowed to stand at a low temperature, although in most cases they contain but little stearin.

Such solid deposits form readily in olive oil, whilst arachis oil becomes nearly solid when chilled. By warming the oils these "stearine" deposits melt, and blend once more with the rest of the oil.

For the separation of these deposits from oils a method of filtration through coarse canvas filters at a low temperature is employed, and the resulting mass is afterwards subjected to moderate pressure to separate the bulk of the remaining fluid oil.

Olive oil which has thus been freed from its more solid glycerides is much less liable to become cloudy in cold weather, and is, therefore, known in commerce as *winter oil.*

Similarly, cotton-seed oil yields a solid fat known as "cotton stearine," whilst lard is separated into a more solid product, "lard stearine," and a liquid oil termed "lard oil."

Coconut oil and palm oil are fractionated by a similar process of slow, steady pressure at a low temperature into their respective "stearines" and "oleines." Coconut stearine thus separated melts at a considerably higher temperature than the original fat, and is used as a substitute for cacao butter.

Separation of Fat from Animal Tissues

The so-called "fat" of animals is composed of cellular tissue in which is deposited the real fat, *i.e.* the glycerides of various fatty acids. In order to separate the fat from the

nitrogenous tissue it is necessary to apply mechanical means, such as pressure, or to rupture the cells by means of heat, so that the oily matter exudes.

The fat of animals varies in consistency not only with the species of animal, but also in different parts of the same animal. Thus, in the case of fish, and marine animals such as the whale, the fat is fluid at the ordinary temperature, and will exude from the tissue as soon as partial decomposition has broken down the cell walls. Advantage is taken of this fact in separating the oil from the livers of cod-fish, sharks, etc., the material being stored for some time before expression.

In land animals the fat is usually most solid in the tissue surrounding the kidney, and most fluid in the deposits on the breast and neck, but in either case the cells require to be ruptured with heat for the commercial extraction of the fat.

Rendering with Water or Steam.—In several of the processes of separating fat from animal tissues the material is first finely divided or crushed between rollers, and then heated with water in a steam-jacketed pan, the fat being skimmed off as it rises to the surface. In order to prevent any decomposition of nitrogenous matter the temperature is kept as low as possible until near the end of the process, when the water is brought to the boiling point. This method of separation yields a white fat of good quality suitable for the manufacture of oleomargarine, but it does not extract the whole of the fat from the tissues.

In some of the methods of dry fusion the material is finely minced and gently heated to a temperature (about 55° C.) just sufficient to melt the fat, which is drawn off and separated into a "stearine" and "oleine" (*supra*). By careful regulation of the temperature in this way no objectionable odours are produced, especially when the freshest material is used, as in the manufacture of food products.

For the complete separation of fat from the tissues, however, temperatures above 100° C. are required, the material being meanwhile mechanically agitated. Under these conditions, the nitrogenous tissue shrivels up and emits

malodorous volatile products, which contaminate the separated fat, so that it is rarely suitable for food.

Rendering of Lard.—It is usual in the American factories to render the different parts of the hog separately, so as to obtain different grades of lard, which are also put up in distinct packages. Thus the best grades are packed in bladders, whilst for other qualities small tubs are used, and the lard contained in them is commercially known as "keg lard." Wiley[1] gives the following classification of the different qualities of American lard—

1. *Neutral Lard*, which is rendered from the absolutely fresh leaf of the pig at a temperature of 104° to 120° F. It contains only about 0·25 per cent. of free fatty acids, and is used almost exclusively in the manufacture of oleomargarine.
2. *Leaf Lard*, which is composed of the fat separated by the heat of steam under pressure from the residue left from the preparation of neutral lard.
3. *Choice Kettle-rendered Lard: Choice Lard.*—This consists of fat from the portions of leaf not used in (1), and of fat from the back, and is rendered in steam-jacketed open kettles.
4. *Prime Steam Lard*, which is separated from the fat of the head, heart, and small intestines. Practically it may represent the fat of the entire animal.
5. *Guts*, which represents the fat from every part of the hog, except the lungs and heart.

The refuse material rendered from animals dying in transit is known as *white* and *brown grease*, and is used in the manufacture of soap and lard oil, whilst *yellow grease* is prepared from the refuse of the packing houses.

Voigtländer[2] describes the differences in the methods of manufacturing American and German lard, the latter being a harder and more crystalline product. As prepared by the Hungarian process, the melted fat is mechanically agitated in a closed vessel until nearly solid, when a small proportion of

[1] U.S. Dept. of Agriculture, Bull. No. 13, Part IV.
[2] *Zeitsch. angew. Chem.*, 1898, 857.

solid lard or lard stearin is added. The final product is known commercially as *pure lard*, and as thus refined keeps its consistency.

Purification of Fats and Oils

Filtration, as described on p. 28, will in many cases render the oil sufficiently free from solid impurities, but in the case of some oils a subsequent treatment with heat or chemical agents is required to remove mucilaginous substances which have also been extracted from the seed.

One method of coagulating the albuminous matter is by the action of steam, which may be injected into the oil. Another process is to force warm water in a fine state of division through the oil, so as to cause the albuminous impurities to separate in the aqueous layer.

Mechanical fining by means of materials such as clay, Spanish earth, fuller's earth, kambara earth, charcoal and similar substances is also frequently employed, the subsiding particles carrying down with them the suspended matter. Or a combined process of heating and mechanical fining may be used.

Various chemical agents, such as sulphuric acid, tannin with gelatin, zinc chloride, and liquid sulphur dioxide are in use for the purification of oils for technical purposes, but these are unsuitable for the treatment of edible oils.

Alkaline refining processes, however, are used in the purification of cotton-seed and other food oils. The crude oil is mixed with the calculated quantity of an alkaline lye and mechanically agitated, either with or without the aid of heat. The alkaline liquid as it subsides removes with it the soaps which it has formed by combination with the free fatty acids and resins in the oil, and the residual oil is washed first with a weaker solution of alkali and then with water. The deposit of "foots" thus separated from the oil is used in the manufacture of soap.

Bleaching Oils.—The methods of bleaching oils and fats include treatment with hot air, artificial light, and with

chemicals such as potassium bichromate, hydrogen peroxide and chlorine; but as these are intended for improving the appearance of technical products, and are not supposed to be used in the preparation of edible oils, details of the processes used may be omitted.

Deodorising Fats.—Certain fresh fats, notably coconut oil, have a pronounced odour due to the presence of volatile fatty acids and other compounds, and, before they can be used for food, it is necessary to eliminate or reduce this odour.

In Schlink's method of deodorisation coconut oil is treated with alcohol and animal charcoal; and the resulting product, which is practically tasteless, is sold as "vegetable lard."

In another process, devised by Ruffin, the coconut oil is first separated into "stearine" and "oleine" (p. 29) by being allowed to stand for several hours at its melting point, and then pressed. The crystalline fraction (coconut stearine) is then treated with lime, evaporated in a vacuum, and freed from the calcium soap and excess of lime by expression. By this treatment the melting point of the fat is raised about 8° C.

Several processes of deodorising coconut oil depend on the removal of the free fatty acids, etc., by means of solutions of alkalis or sodium silicate, followed by filtration or decantation.

However thoroughly coconut oil has been deodorised, there is always a tendency for the characteristic odour to reappear after the fat has been exposed to the air.

Removal of Rancidity.—The development of rancidity is attended by the formation of free fatty acids; and by removing these by treatment with alkalis or the like the flavour and odour of a rancid fat are materially improved (*see* p. 7).

The numerous processes which have been patented for this purpose include treatment with alcohol, with solutions of sodium bisulphite, animal charcoal, prepared chalk, milk of lime, etc., with or without the accompaniment of a current of steam to expel the aldehydes and other volatile substances

which are invariably produced when a fat becomes rancid (*see* p. 8).

The treatment can only be regarded as effecting a temporary improvement, for fats which have thus been "sweetened" will not keep as well as fresh fats.

Extraction of Oil by Means of Solvents

The methods of extracting oil by treating the material with a suitable solvent, such as carbon bisulphide, petroleum spirit, or carbon tetrachloride, are extensively used in the preparation of oils for technical purposes, but are hardly suitable for the preparation of edible oils, since substances other than oil are also extracted.

Thus, processes of this kind are used for removing the residual oil from oil-cake obtained as described above, whilst crushed seeds of various kinds are extracted to obtain oils for paint and similar technical purposes.

Essentially the most simple type of apparatus consists of a closed cylinder with a perforated false bottom, on which is placed the meal or crushed seed, whilst the hot solvent is introduced, either at the top or the bottom, and, percolating through the material, is drawn off by a pump and made to circulate through the cylinder again: this process being continued until the whole of the oil has been extracted. The solvent is then conducted through similar cylinders containing more material, and finally to a still where the solvent is evaporated, leaving a residue of oil.

CHAPTER IV

METHODS OF EXAMINATION

THE methods of examining oils and fats are based (1) upon the determination of certain physical characters, such as the specific gravity and the melting point: (2) on certain chemical properties, such as the amount of iodine or bromine absorbed under definite conditions; and (3) on the identification or isolation of specific compounds in the oils, such as sesamol in sesamé oil, or arachidic acid in arachis oil.

I.—PHYSICAL METHODS

The Specific Gravity

The specific gravity of oils is conveniently determined by means of a Sprengel tube, the weight of the definite volume of oil being compared with that of water at 15·5° C. In the case of solid fats it is usual to take the specific gravity of the melted material at the temperature of boiling water compared with water at 15·5° C. Special hydrometers for determining the specific gravity of oils are sold, but the method gives less accurate results than those obtained by weighing the oil.

When the results obtained at one temperature are to be calculated to a standard temperature, it is necessary to take into account the rate of expansion of the oil.

The correction to be applied for a difference of 1° C. varies with the particular oil or fat. For example, Allen found that the rate of expansion of cotton-seed oil was 0·629 and that of whale oil 0·697 for each 1° C.

Wright[1] has calculated the average value for the expansion of any oil or fat, so that a correction may be rapidly applied in any special instance. The results obtained by the use of his equation are embodied in the following table, which gives the correction to be applied to the specific gravity for each variation of 1° C. from the standard temperature (15·5° C.).

° C.	Factor.	° C.	Factor.
10	0·99611	18	1·00177
11	0·99682	19	1·00248
12	0·99752	20	1·00319
13	0·99823	21	1·00391
14	0·99894	22	1·00462
15	0·99965	23	1·00534
16	1·00035	24	1·00605
17	1·00106	25	1·00677

Typical specific gravities of the more important edible oils and fats will be found in the tables of values in Chapters V and VI.

The Melting and Solidification Points

In order to obtain concordant and trustworthy results it is essential that the determination of the melting point should be made under constant conditions. The method commonly used is to draw a little of the melted fat into a capillary tube, which is then allowed to stand for several hours, preferably at least twelve, before it is attached to the bulb of a thermometer. The latter is immersed in water which is heated very gradually, with constant stirring, until the point is reached where the fat melts, and rises in the capillary tube. This is taken as the melting point.

In other methods the softening point is determined, either by noting the temperature at which the fat falls to the bottom of a closed capillary tube, or the point at which it detaches itself from the bulb of the thermometer.

[1] *J. Soc. Chem. Ind.*, 1907, xxvi, 513.

The melting point of mixtures of two solid fatty acids affords an approximate estimation of the composition of the mixture.[1]

The solidification point is in many respects more accurate than the melting point, since larger quantities of material are used and errors due to impurities are thus reduced. Various modifications of Dalican's original process are used in different countries, but these differ in the method of preparing the fatty acids and of heating them rather than in principle. In brief, the method consists in melting the dried fatty acids and cooling them very gradually in a tube which is surrounded by an air space (a larger tube or bottle). As soon as solidification begins the fatty acids are stirred with a circular motion first three times to the right and then three times to the left. After falling, the mercury of the thermometer suddenly rises to a point at which it remains stationary for about two minutes, and this temperature is taken as the solidification point.

This method of determining the solidification point is commercially known as the "titer test."

The use of a vacuum jacketed tube, as suggested by Shukoff,[2] enables the cooling of the fatty acids to be effected very slowly, and tends to make the results more accurate.

Double Melting Point of Glycerides.—Certain fats show two distinct melting points, a phenomenon which has some bearing on the determination of the melting point of glycerides. For example, when tallow is heated for a short time at a temperature above its melting point and then cooled it will melt at, say, about 35° C. If it is then re-melted at this temperature, and again cooled, it will melt at a temperature considerably higher than the original melting point.

The mixed glycerides, which have been isolated from natural fats or synthetically prepared, show this phenomenon of a double melting point to a pronounced extent. The

[1] See Hehner and Mitchell, *Analyst*, 1896, xxi, 319.
[2] *Chem. Rev. Fett Ind.*, 1899, vi, 11.

explanation has been given by Grün and Schacht,[1] who found that in such cases two isomeric modifications of the glycerides are present, each of which has a different melting point, and that there is a gradual transformation of the modification of lower melting point into that of higher melting point.

In the case of symmetrical triglycerides showing two melting points the maximum difference between the two temperatures was found by Grün[2] to be 16° C.

The liquid form of such glycerides appears to be produced by the super-cooling of the solid modification while in the melted condition.

Thermal Tests

The unsaturated compounds in fats combine with certain reagents so rapidly that it is possible to measure the heat of the reaction.

Maumené Test

The first method of this kind was devised by Maumené,[3] who found that it was possible to distinguish between different oils by the difference in the heat evolved on treating them with sulphuric acid under constant conditions. For example, the temperature of olive oil rose 42° C., whilst that of linseed oil rose 103° C.

The method will give concordant results if the conditions of working and the strength of acid used are identical, but slight variations in the factors have a great influence upon the results.

To prevent charring of the mass, Ellis[4] made an addition of mineral oil to the mixture; but carbon tetrachloride, as proposed by Mitchell,[5] is the most suitable diluting agent.

By dissolving the oil in this solvent and adding sulphuric

[1] *Ber.*, 1907, xl, 1778.
[2] *Ibid.*, 1912, xlv, 3691.
[3] *Compt. rend.*, 1852, xxxv, 572.
[4] *J. Soc. Chem. Ind.*, 1886, v, 161.
[5] *Analyst*, 1901, xxvi, 169.

acid of definite strength, the heat evolved with sulphuric acid is in most cases proportional to the iodine value, or, in other words, the Maumené figure is usually a measure of the degree of unsaturation of the oil.

The Bromine Thermal Test

A rapid method of estimating the iodine value of most unoxidised fats and oils was based by Hehner and Mitchell[1] upon the fact that the heat evolved on treating a solution of the fat in chloroform or carbon tetrachloride with bromine is proportional to the amount of iodine absorbed by Hübl's or Wijs' methods.

A small Dewar vacuum tube forms a convenient calorimeter for this purpose, and the apparatus should be standardised by means of several oils and fats, preferably of the same kind as those to be examined. The ratio between the iodine values of these and the rise of temperature will give a factor, which when multiplied by the rise of temperature obtained with a similar fat under identical conditions will give a result in close approximation to the iodine value of the latter.

If, for example, 1 grm. of lard is dissolved in 10 c.cm. of chloroform, the temperature of the solution taken, 1 c.cm. of bromine added from a pipette, and the mixture stirred with the thermometer, a rise of, say, 11·5° C. may be observed. Assuming then that the ratio between the rise of temperature, observed in the same apparatus with a number of lards, and their iodine values was 5·5, the iodine value of the hypothetical sample will be—

$$11{\cdot}5 \times 5{\cdot}5 = 63{\cdot}25$$

The method does not give good results in the case of fats which are oxidised, since in such cases substitution as well as addition of bromine takes place.

Modifications of the process have been devised by Wiley[2] and by Gill and Hatch,[3] but these lack the simplicity of the original process, and are not more accurate.

[1] *Analyst*, 1895, xx, 146.
[2] *J. Amer. Chem. Soc.*, 1896, xviii, 378.
[3] *Ibid.*, 1899, xxi, 27.

In a recent modification of the method Marden[1] calculates the heat capacity of the apparatus and of the mixture of bromine solution and oil, multiplies their sum by the rise of temperature observed, and divides the result by the grammes of oil used. He thus obtains the results in calories per gramme of oil.

In most instances the results were proportional to the iodine value, but in the case of Chinese wood oil, and some other oils containing hydroxy compounds, there was a pronounced discrepancy, which was attributed to substitution by the bromine.

The bromine thermal method may therefore be regarded as a valuable preliminary test for unoxidised oils of the kind which have already been tested with the same apparatus and method of working.

Solubility Tests

The behaviour of oils towards certain solvents forms a means of distinguishing between some of them. For example, castor oil, which contains hydroxylated acids, is readily soluble in alcohol, but is nearly insoluble in petroleum spirit, whereas in the case of most oils and fats the reverse is the case.

The Valenta Test

A method of differentiating oils was based by Valenta[1] upon the difference in their solubility in acetic acid. For example, rape-seed oil dissolves incompletely and separates out from the solution at a high temperature, whereas butter fat remains dissolved until the acid has been chilled to a much lower temperature. The Valenta figure is the temperature at which a solution of a definite quantity of the fat in a definite amount of acetic acid of a standard strength becomes turbid when gradually cooled.

Obviously the results will vary considerably with slight variations in the strength of the acetic acid, and this draw-

[1] *J. Ind. Eng. Chem.*, 1916, viii, 121; *Analyst*, 1916, xli, 176.
[2] *Dingler's Polyt. J.*, 1884, cclii, 296.

back is not altogether obviated in the modification of the test devised by Chattaway, Pearmain and Moor.[1]

The applicability of the test to the analysis of butter is also discussed by Jones.[2]

Critical Temperature of Solution

A method, which is free from some of the defects of the Valenta test is that devised by Crismer,[3] which consists in dissolving the oil in a solvent, such as alcohol, under pressure in a sealed tube, and noting the temperature at which the liquids separate when the solution is slowly cooled.

This *critical temperature of solution* varies with the amount of insoluble fatty acids in a fat, and in the case of mixtures, is approximately the arithmetical mean of the values of the constituents.

Rancid fats give lower values than fresh fats, but, on neutralising the free fatty acids with sodium carbonate and washing the residue, the neutral fat will give normal figures. Asboth[4] confirmed the value of the method as a rapid preliminary test in the analysis of butter.

OPTICAL EXAMINATION

Absorption Spectra.—Many oils, particularly those of vegetable origin, show a spectrum with characteristic absorption bands, although, as these are mainly due to chlorophyll and impurities, they tend to disappear when the oil is refined. In some cases, however, the test is useful for detecting the presence of vegetable oil in animal oils, and a special apparatus for the test was devised by Patterson.[5]

Refractive Power.—A much more valuable optical method of examining fats is based on the observation of their refractive index. For this purpose the Abbé-Zeiss refractometer is commonly employed. The results are expressed in arbitrary

[1] *Analyst*, 1894, xix, 147.
[2] *Ibid.*, 151.
[3] *Ibid.*, 1895, xx, 257; 1896, xxi, 241.
[4] *Ibid.*, 1897, xxii, 21.
[5] *J. Soc. Chem. Ind.*, 1890, ix, 36.

figures, but are capable of being expressed in terms of the refractive index if required. It is essential in stating the results obtained with this instrument that the temperature of observation should also be given. A method of avoiding errors in calculating the results was devised by Richmond.[1] In the case of Jean's oleorefractometer,[2] the results are expressed in the terms of an arbitrary scale based on the refractive index of a standard oil (sheep's-foot oil), supplied with the instrument. If the oil under examination has the same refractive power as that of the standard oil there will be no deviation in the ray of light, but otherwise any deviation to the right or left is measured upon a scale. The application of this instrument was studied by Pearmain.[3]

II.—CHEMICAL METHODS

The chemical methods used in the examination of fats and oils are based upon the differences in the characteristics of the various fatty acids or othe constituents which they contain. Some of the methods, such as the determination of the Reichert-Meissl value, are purely empirical, but in other cases, such as the estimation of arachidic acid in arachis oil, a compound more or less specific to the oil is quantitatively separated.

In the routine analysis of oils and fats certain constants or values are usually determined, and it is possible by comparing the results obtained with those recorded for genuine oils to form an opinion as to the character of the sample in question.

THE ACID VALUE

When freshly expressed from the seed or fruit, vegetable oils contain only a small proportion of free fatty acids. But, owing to the presence of enzymes in the seed and the action of air and light, the hydrolysis of the glycerides may proceed rapidly, so that the oil soon becomes inedible from the liberation of free fatty acids.

[1] *Analyst*, 1907, xxii, 44.
[2] *Compt. rend.*, 1889, cix, 616.
[3] *Analyst*, 1895, xx, 135.

The acidity of a fat is determined by shaking a small weighed quantity of the sample with hot alcohol, and titrating the liquid with standard sodium or potassium hydroxide, with phenolphthalein as indicator.

The results may be expressed in terms of the predominant fatty acid, usually oleic acid, but they are more frequently calculated into the number of milligrammes of potassium hydroxide required to neutralise 1 grm. of the fat.

The result thus expressed is known as the *acid value*, and may be readily calculated into the corresponding quantity of free fatty acids expressed as oleic acid, palmitic acid, etc.

Olive oils often contain 4 to 5 per cent. of free acids, whereas cotton-seed oils, which are submitted to a refining treatment with alkali, are usually nearly neutral. In the case of coloured edible fats it is advisable to separate the colouring matter prior to determining the acid value.

Since the proportion of free fatty acids depends upon so many external factors, the acid value cannot be regarded as a distinctive constant of a fat, but it is an essential point in judging of the suitability of a fat for food.

Saponification Value

This term signifies the number of milligrammes of potassium hydroxide required to saponify completely 1 grm. of a fat or oil.

This method was first devised by Koettstorfer[1] for the analysis of butter, and is still carried out in essentially the original manner. A weighed quantity (1·5 to 2 grms.) of the fat is boiled beneath a reflux condenser with 25 c.cm. of a standard solution (about N/2) of potassium hydroxide in purified alcohol, the flask being shaken from time to time. After about thirty minutes, when all fat has dissolved, the excess of alkali is titrated with standard hydrochloric acid whilst at the same time a similar quantity of the alcoholic alkali is also titrated. The difference between the two results corresponds with the alkali which has entered into combination with the fat.

[1] *Zeitsch. anal. Chem.*, 1879, xviii, 199.

A method of cold saponification was devised by Henriques,[1] and may be found convenient when a large number of estimations is required.

The following table gives the saponification values of some of the principal triglycerides:—

Glyceride.	Saponification Value.	Saponification Equivalent.
Tributyrin	557·3	100·7
Trilaurin	263·8	212·7
Tripalmitin	208·8	268·7
Tristearin	189·1	296·7
Triolein	190·4	294·7
Trierucin	160·0	350·7
Trilinolin	191·7	292·7
Triricinolein	180·6	310·7

The mean equivalent weight of the fat corresponding the amount of potassium hydroxide used is known as *saponification equivalent.* It is calculated by means of the formula—

$$x = \frac{56,100}{S}$$

where S represents the saponification value.

The saponification values of some of the principal edible oils and fats are as follows:—

Oil.	Saponification Value.	Oil.	Saponification Value.
Arachis oil	186–195	Maize oil	186–193
Almond oil	189·5–192	Mutton tallow	196
Beef fat	196–200	Nut oil	190–197
Butter fat	221–230	Olive oil	185–196
Cacao butter	192–195	Palm oil	200–202
Coconut oil	254–262	Palm-kernel oil	248
Cotton-seed oil	191–196	Poppy-seed oil	193–195
Lard	195–203	Sesamé oil	188–193
Linseed oil	188–195	Sunflower oil	188–193

[1] *Zeit. angew. Chem.*, 1895, 721; 1896, 221; *Analyst*, 1896, xxi, 67, 192.

The Ester Value.—Since the acid value measures the amount of free fatty acids in a fat, and the saponification value the total amount of potassium hydroxide required to neutralise the free fatty acids and to hydrolyse the glycerides, the difference between the two values affords a measure of the proportion of glycerides or other esters in a fat. It is commonly termed the *ester value*, and is chiefly used in the examination of beeswax.

Neutralisation Value of Fatty Acids.—The fatty acids liberated from an oil or fat will combine with various proportions of potasssium hydroxide according to their character. The amount required to convert them into potassium soaps (*i. e.* their saponification value) is usually described as their neutralisation value.

THE HEHNER VALUE

This test takes its name from Hehner, who was the first to differentiate between different kinds of fat by estimating the amount of fatty acids insoluble in hot water which each contained.

In the case of the majority of fats only small amounts of soluble fatty acids are present, and the proportion of insoluble fatty acids will approximate closely to the total proportion (95 to 96 per cent.). But in the case of butter fat, coconut oil, palm-kernel oil and some other fats, the percentage of insoluble fatty acids is much lower. Thus, Hehner values of 85 to 89·6 have been recorded for butter fat, and of 82·3 to 90·5 for coconut oil.

In mixtures of butter fat with fats other than coconut or palm-kernel oils it is possible to calculate the proportion of foreign fat by means of the formula—

$$x = (H - 87{\cdot}5) \times 12{\cdot}5,$$

where H represents the observed Hehner value, and 87·5 is assumed to be the average Hehner value of butter fat. Obviously the extending use of coconut oil and similar fats for margarine renders this calculation untrustworthy in many cases.

THE REICHERT-MEISSL VALUE

This is the measure in c.cm. of N/10 alkali solution of the proportion of volatile fatty acids distilled in a current of steam under constant conditions from 5 grms. of the oil or fat saponified and acidified under specified conditions.

The test was originally devised by Reichert,[1] and modified by Meissl.[2]

Of the various other modifications suggested, reference may be made to that of Wollny,[3] who devised precautions to prevent the disturbing influence of carbon dioxide, and to that of Leffmann and Beam,[4] who recommended the use of a glycerin solution of sodium hydroxide to reduce the possibility of the formation of volatile acids by the action of the alkali on the alcohol.

Kirschner's Extension of the Reichert Process.—Kirschner[5] extended the Reichert process in such a way as to distinguish between the amounts of caprylic and butyric acids. His process is based upon the fact that silver caprylate is insoluble, whilst silver butyrate is soluble in water. The titrated distillate is shaken with 0·5 grm. of silver sulphate, and allowed to stand for an hour before filtration. The filtrate is distilled under specified conditions, the distillate filtered, and 100 c.cm. titrated with N/10 barium hydroxide solution, the results being expressed in the number of c.cm. required by 5 grms. of the fat.

The percentage of butter fat is calculated by means of the formula—

$$4{\cdot}319S - 0{\cdot}456R - 2{\cdot}15,$$

and the percentage of coconut oil by the formula—

$$7{\cdot}42R - 8{\cdot}116S - 3{\cdot}57,$$

where R represents the Reichert-Meissl value, and S the value obtained in the second titration by Kirschner's method.

1 *Zeitsch. anal. Chem.*, xviii, 68.
2 *Dingler's Polyt. J.*, ccxxxiii, 229.
3 *Analyst*, 1887, xii, 203.
4 *Ibid.*, 1891, xx, 153.
5 *Ibid.*, 1905, xxx, 205.

Revis and Bolton[1] have studied this method and find that it may be advantageously used in combination with Polenske's method, and with the method of Shrewsbury and Knapp.

THE POLENSKE VALUE

This affords a measure of the volatile insoluble fatty acids which distil in the determination of the Reichert value.

To obtain concordant results it is essential that the details as to the dimensions of the apparatus and method of working prescribed by Polenske[2] should be exactly followed, since the method gives only the proportion of volatile insoluble acids obtained under empirical conditions.

The insoluble volatile fatty acids left on the filter and in the condenser, etc., after determining the Reichert-Meissl value are dissolved in alcohol, and the solution titrated with N/10 barium hydroxide solution, with phenolphthalein as indicator. The number of c.cm. required is the Polenske value. Since coconut oil contains a much higher proportion of insoluble volatile fatty acids than butter fat, the Polenske value of the former will be much higher. For example, Polenske[3] found that 31 samples of butter fat, having Reichert-Meissl values of 23·3 to 30·1, showed Polenske values of 1·5 to 3·0; whereas four samples of coconut oil, with Reichert-Meissl values of 6·8 to 7·7, gave Polenske values of 16·8 to 17·8.

The value of the method has been confirmed by Revis and Bolton, who give the following table of the Reichert-Meissl and corresponding Polenske values—

Reichert-Meissl Value	32	31	30	29	28	27	26	25	24	23
Polenske Value	3·5	3·2	3·0	2·9	2·7	2·4	2·0	1·8	1·7	1·6

In their experience, if a butter fat gives a Polenske value exceeding by 0·5 c.cm. the figure corresponding to the Reichert-Meissl value the presence of coconut oil or palm-kernel oil is indicated.

[1] *Analyst*, 1911, xxxvi, 336. [2] *Ibid.*, 1904, xxix, 154.
[3] *Ibid.*, 1911, xxxvi, 333.

The Iodine Value

The chemical reactions involved in the addition of iodine or other halogen to unsaturated fatty acids or glycerides have already been described.

The percentage of iodine or equivalent halogen with which an oil is capable of combining is known as its *iodine value.*

The rate of absorption of pure iodine from an alcoholic solution is too slow for practical purposes, and for this reason was discarded by Hübl, who used instead a mixture of a solution of iodine with a solution of mercuric chloride, the amount of the absorption being calculated in terms of iodine.

Hübl's Reagents.—(*a*) Iodine, 50 grms. dissolved in 1 litre of 95 per cent. alcohol; (*b*) mercuric chloride (60 grms.) in 1 litre of alcohol. The solutions are kept separate and mixed shortly before use. To obtain trustworthy results it is essential to add a large excess of the reagent, and to allow the mixture to stand for at least seven hours, especially in the case of oils, such as linseed oil, which have high iodine values.

The active agent in Hübl's reaction appears to be iodine monochloride, which is produced on mixing the two solutions.

For a discussion of the theory of the process see Lewkowitsch,[1] and Schweitzer and Lungwitz.[2]

Wijs' Method.—Wijs[3] concluded that hypoiodous acid is the chief agent in the iodine absorption, and to prevent its decomposition he made use of it in the nascent form by dissolving iodine chloride in glacial acetic acid, which contained only sufficient water to decompose the iodine chloride—

$$ICl + H_2O = HCl + HIO.$$

His reagent was prepared by dissolving 13 grms. of iodine in 1 litre of glacial acetic acid, and introducing chlorine until the amount of thiosulphate required by the liquid was doubled.

The method now commonly used is to dissolve 7·14 grms. of iodine and 9·36 grms. of iodine trichloride in a litre of acetic acid.

[1] *Analyst*, 1899, xxiv, 257.
[2] *J. Soc. Chem. Ind.*, 1895, xiv, 130, 1030.
[3] *Ber.*, 1898, xxxi, 750.

Dubovitz[1] has shown that this proportion is incorrect and that the solution should contain 8·5 grms. of iodine and 7·8 grms. of iodine trichloride.

Ueno,[2] however, has found that solutions containing such an excess of chlorine give results practically identical with those obtained with a "normal" solution.

In the case of oils such as olive oil, Wijs' solution gives, within a few minutes, results in agreement with those obtained by Hübl's method. When applied to highly unsaturated oils, such as linseed oil, higher but more trustworthy values are obtained than by the older method.

Hanus' Iodine Bromide Solution.—This is prepared by dissolving 10 grms. of iodine bromide in 500 c.cm. of glacial acetic acid. The reagent is allowed to act for 15 minutes on a solution of 0·1 to 0·7 grm. of the oil in chloroform, and, after the addition of potassium iodide, the liquid is titrated with standard sodium thiosulphate solution.[3] The results agree closely with those given by Wijs' method.

The Bromine Value

Bromine is absorbed by oils and fats much more rapidly than iodine, so much so that in many cases it is possible to determine the iodine value by measuring the heat of bromination (*see* p. 39).

If care be taken to prevent the heat of reaction rising too high, the bromine value corresponds closely with the iodine value. In the case of some oils, however, which have undergone oxidation a considerable amount of bromine combines by substitution, in addition to that which is added on to the unsaturated bonds.

McIlhiney[4] devised a method of measuring both the amount of bromine which combined by substitution and that combining by addition.

The bromine substitution value of most oils and fats ranges

[1] *J. Soc. Chem. Ind.*, 1915, xxxiv, 305.
[2] *Ibid.*, 1916, xxxv, 367.
[3] *Z. Unters. Nahr. Genussm.*, 1901, iv, 913.
[4] *Analyst*, 1894, xix, 106; *ibid.*, 1899, xxv, 106.

from about 0·3 to 3·6. The method was subsequently studied by Williams,[1] who gave comparative results obtained by it and by Wijs' iodine chloride method.

Hehner's gravimetric bromine method[2] is useful in the case of certain oils and fats with low iodine values, but is open to the objection that the temperature required to expel the excess of bromine is liable to cause an increased degree of substitution.

THE INSOLUBLE BROMIDE TEST

A method of distinguishing between certain kinds of oils was based by Hehner and Mitchell[3] upon the fact that some when dissolved in ether and treated with a slight excess of bromine yield a considerable amount of an insoluble bromide.

For example, linseed oil usually yields about 24 to 25 per cent. of this compound, which appears to be the bromide of a mixed glyceride, melting at 143·5 to 144° C., and containing about 56 per cent. of bromine.

Similar bromides are given by marine animal oils, but these blacken when heated, a property which enables these oils to be detected in vegetable oils.

Walnut oil yields under 2 per cent. of insoluble bromide, whilst candle-nut oil yields 7 to 8 per cent.

The amounts of bromide thus obtained from various fish oils are given by Walker and Warburton[4] and by Procter.[5]

The test affords a valuable means of estimating the approximate proportion of linseed oil in admixture with other vegetable oils.

THE ACETYL VALUE

This test, devised by Benedikt and Ulzer, is based upon the fact that when a fatty acid or alcohol containing an alcoholiform hydroxy group is treated with acetic anhydride an acetyl derivative is produced.

1 *J. Soc. Chem. Ind.*, 1900, xix, 300.
2 *Analyst*, 1895, xx, 47, 277.
3 *Ibid.*, 1898, xxiii, 315.
4 *Ibid.*, 1902, xxviii, 237.
5 *J. Soc. Chem. Ind.*, 1906, xxv, 798.

Thus, in the case of hydroxystearic acid the following reaction takes place—

$$C_{17}H_{34}<\begin{matrix}OH\\CO{\cdot}OH\end{matrix}+\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}>O=C_{17}H_{34}<\begin{matrix}O{\cdot}C_2H_5O\\CO{\cdot}OH\end{matrix}+C_2H_4O$$

The excess of acetic anhydride may be removed by washing the product with water.

The term *acetyl value* is used to denote the weight of potassium hydroxide neutralised by 1000 parts of the acetylated product.

The sources of error in this original method were pointed out by Lewkowitsch,[1] who subsequently devised a more accurate method of determining the value.[2]

In a further communication[3] he pointed out that the acetyl value might be due to the following causes: (1) Hydroxy acids; (2) free alcohols; (3) oxidised fatty acids; (4) acids of unknown composition; (5) mono- and di-glycerides; and (6) rancidity.

Castor oil has an acetyl value of about 150, whilst the values of other oils and fats range from about 2 (coconut oil) to 15 (cotton-seed oil) and 19 (croton oil).

Separation of Solid from Liquid Fatty Acids

The method most commonly used for the separation of liquid and solid fatty acids is based upon the observation first made by Varrentrapp that lead oleate is readily soluble in ether, whereas lead palmitate and lead stearate are only sparingly soluble.

A modification of this method was described by Rose,[4] whilst Muter and de Koningh[5] simplified the process and devised a special form of apparatus for drawing off an aliquot portion of the ethereal solution.

Unfortunately this method only effects a partial separation of the two kinds of acids, since the solid fatty acids will still

[1] *Proc. Chem. Soc.*, 1890, vi, 72, 91.
[2] *J. Soc. Chem. Ind.*, 1897, xvi, 503.
[3] *Analyst*, 1899, xxiv, 319.
[4] *J. Soc. Chem. Ind.*, 1887, vi, 306.
[5] *Analyst*, 1889, xiv, 61.

contain a certain amount of liquid fatty acids, whilst part of the solid acids will be dissolved by the ether.

At best, the method effects a fractionation and a concentration of the fatty acids, although it is useful for the estimation of individual constituents (*see* Arachis Oil) and for the examination of oils which are suspected to be adulterated with more unsaturated oils.

In Farnsteiner's[1] method benzene is used as the solvent for the lead salts, and the temperature is maintained at 8° to 12° C., but even in this modification the results are not quantitative.

Another method of separating the fatty acids is that of Partheil and Ferié,[2] which is based upon the pronounced differences in the solubilities of the different lithium salts in alcohol.

Thus, 100 c.cm. of alcohol of specific gravity 0·797 dissolved at 18° C. the following amounts of the lithium salts of: Lauric acid, 0·418; myristic acid, 0·184; palmitic acid, 0·0796; stearic acid, 0·041, and oleic acid, 0·9804 grm.

Estimation of Stearic Acid

Hehner and Mitchell[3] based a method of estimating stearic acid in a mixture of fatty acids upon the principle that a solvent already saturated with pure stearic acid will not dissolve any further quantity, but will dissolve other fatty acids.

Alcohol is a suitable solvent for the purpose. It is saturated with pure stearic acid at 0° C., and weighed quantities of the fatty acids are dissolved in this solution, and exposed in an ice-chest to a temperature of 0° C. for twelve hours. The liquid is then drawn off through a thistle funnel covered with wash-leather, the deposit washed with the ice-cold saturated solvent, and then dried at 100° C. and weighed. An allowance is made for the stearic acid in the solvent which clings to the side in the washing process.

[1] *J. Soc. Chem. Ind.*, 1898, xvii, 804.
[2] *Analyst*, 1904, xxix, 51.
[3] *Ibid.*, 1896, xxi, 316.

From an experimental investigation of this method Holland, Reed and Buckley[1] conclude that supersaturation of the solution may readily occur owing to the presence of insufficient stearic acid. To obviate this they add a weighed quantity of pure stearic acid to the melted fatty acids under examination, and deduct this from the weight of the deposit. By this means it is possible to counteract to a large extent the solvent action of palmitic acid.

In this way they found butter fat to contain from 7 to 22 per cent. of stearic acid.

SEPARATION OF CHOLESTEROL AND PHYTOSTEROL

A method of distinguishing between animal and vegetable fats is based upon the fact that the former contain cholesterol, and the latter phytosterol (p. 23). These alcohols may be obtained in crystalline form by dissolving the unsaponifiable matter of the fat in ether, allowing the solution to evaporate, drying the residue on the water-bath, and crystallising it from absolute alcohol.

The crystals of the two alcohols show a distinct difference in form, but in the case of mixtures of animal and vegetable fats the results are often indecisive.

Phytosteryl Acetate Test.—The crude crystals from the alcoholic solution are heated with 2 to 3 c.cm. of acetic anhydride, the excess of which is subsequently evaporated on the water-bath, and the residue recrystallised from absolute alcohol.

The crystals of cholesteryl acetate melt at 114·5° C., whilst those of phytosteryl acetate melt at 125·6 to 137° C., and they differ in their crystalline form. By continuing the recrystallisation it is possible to ascertain by the melting point whether any phytosteryl acetate is present in the crystals separated from an animal fat.[2]

Digitonin Method.—A rapid method of separating cholesterol and phytosterol from oils and fats is to treat the

[1] *Analyst*, 1916, xli, 209.
[2] See Bömer, *J. Soc. Chem. Ind.*, 1902, xxi, 192.

mixed fatty acids with digitonin, which precipitates characteristic digitonides of the alcohols.[1]

As part of the phytosterol is present in vegetable fats in the form of an ester it is better to saponify the oil before the precipitation,[2] although these alcohols, so far as they are present in the free condition, can be precipitated directly from the fats themselves.

In a simple modification of the process the melted fat (50 grms.) is stirred for five minutes at 60° to 70° C. with 20 c.cm. of a 1 per cent. alcoholic solution of digitonin, and the mass filtered with the aid of suction, chloroform being added to the hot solution, if necessary. The residue of digitonide is washed with six successive portions of 5 c.cm. of ether, dried for five minutes at 30° to 40° C., and dissolved in 2 c.cm. of hot acetic acid, and the solution boiled for five minutes in a test-tube fitted with a vertical tube to act as condenser, and then filtered through cotton-wool. The tube and filter are washed with two portions (0·5 c.cm. each) of hot absolute alcohol, the filtrate and washings evaporated, and the residue of phytosteryl or cholesteryl acetate examined as described above.

ALCOHOLYSIS OF GLYCERIDES

On heating an oil or fat with an alcohol, such as methyl or ethyl alcohol, in the presence of an acid, decomposition takes place, with the formation of the fatty acid esters of the alcohol. These esters may be separated by treating the alcoholic solution with an excess of water or salt solution, and their composition may be determined by fractional distillation under reduced pressure.

This method was shown by Haller[3] to afford useful information as to the composition of an oil, and was applied by Haller and Youssoufian[4] to ascertain the composition of

[1] Windaus, *Analyst*, 1910, xxxv, 256; 1914, xxxix, 32, 310; 1915, xl, 506.

[2] Klostermann and Opitz, *Analyst*, 1916, xli, 317.

[3] *Compt. rend.*, 1906, clxxiii, 657.

[4] *Ibid.*, 803.

coconut oil, and by Mayer[1] to determine that of cotton-seed oil.

It has been critically studied by Elsdon,[2] who finds that it may be useful in ascertaining the approximate composition of a fat, but that it is too slow for ordinary practice, whilst the results are not quantitative.

Tests of Drying Capacity

The term *drying*, as applied to oils, is used to denote a process of oxidation accompanied by some polymerisation, which causes a varnish-like film to be produced.

In general, the proportion of linolic and particularly linolenic acids, has a great influence upon the drying properties, so that in the case of vegetable oils the iodine value affords an indication of the drying capacity. But this does not apply to other classes of oils, since cod-liver oil and other fish and marine animal oils have high iodine values, without any very pronounced drying properties.

On the basis of their behaviour when exposed in thin films to the air, vegetable oils are usually classified into *non-drying*, *semi-drying* and *drying oils;* the first group being typified by olive oil, the second by cotton-seed oil, and the third by linseed oil.

This classification, however, is only a rough one, and many oils might be classified in more than one group. In fact, the property of "drying" is a question of degree rather than of a distinct difference in behaviour.

One method of determining the drying capacity is to expose a thin film of the oil upon a glass plate for twelve to twenty-four hours in an oven at 100° C., and to note the condition of the film at the end of the time.

More quantitative results are obtained, however, by means of Livache's test,[3] in which the oil is mixed with finely divided lead, and exposed to the air until it ceases to gain

[1] *Chem. Zeit.*, 1907, xxxi, 793.
[2] *Analyst*, 1913, xxxix, 8.
[3] *Comptes rend.*, 1886, cii, 1167.

materially in weight. This test is useful for detecting the presence of linseed or cotton-seed oils in olive oil.

A still more rapid absorption of oxygen may be effected by mixing the oil with manganese resinate and precipitated silica, as suggested by Bishop.[1]

The Elaidin Test

The conversion of acids and glycerides of the oleic acid series into isomeric compounds under the influence of nitrous acid has been described previously (p. 17).

Since oils rich in oleic acid form a much harder product in the reaction than those which contain a large proportion of more unsaturated fatty acids, it is possible to distinguish between oils of different types by means of this test.

For example, oils such as olive, almond, arachis and lard oil yield hard solid masses; cotton-seed oil, sesamé oil, sunflower-seed oil and whale oil give a pasty mass which separates from a fluid portion; whilst linseed, hempseed and nut oils give no solid product.

A convenient method of applying the test is that described by Archbutt.[2]

Farnsteiner[3] attempted to make the test quantitative, but did not succeed in obtaining more than about 86 per cent. of elaidic acid from oleic acid. Other investigations of the value of the reaction were made by Edmed[4] and by Lidow.[5]

The test is most frequently used in the examination of olive oil, the presence of cotton-seed oil or the like, interfering with the solidification and giving an orange or red-coloured elaidin.

[1] *J. Pharm. Chim.*, 1896, v, 55.
[2] *J. Soc. Chem. Ind.*, 1886, v, 303.
[3] *Ibid.*, 1899, xviii, 500.
[4] *Proc. Chem. Soc.*, 1899, xv, 190.
[5] *Analyst*, 1895, xx, 178.

CHAPTER V

CHARACTERISTICS OF INDIVIDUAL EDIBLE OILS

ALMOND OIL

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Hehner Value.	Iodine Value.	Refractive Index at 15.5° C.	Fatty Acids.		
					Melting Point ° C.	Solidification Point ° C.	Iodine Value of Liquid Fatty Acids.
0·9175–0·9195	189·5–192	96·2	93–101·5	1·4728	13–14	9·5–11·8	101·7

ALMOND oil is obtained by expressing the kernels of bitter, or more rarely of sweet, almonds, *Prunus amygdalus* (*amara* or *dulcis*), which yield about 40 per cent. of oil.

The oils derived from the two varieties of almonds are practically identical in their physical and chemical characters.

Almond oil consists principally of olein, with about 6 per cent. of linolin, and a small amount of glycerides of solid fatty acids.

It does not readily become rancid, probably owing to the small proportion of the more unsaturated fatty acids which it contains.

The oils chiefly used for adulterating almond oil are peach-kernel and apricot-kernel oils. These are both characterised by having higher iodine values than the average figure for almond oil, but in case of admixtures the analytical figures are inconclusive. Colour reactions which have been

suggested will serve to distinguish the oils from one another, but are not trustworthy for the detection of an admixture.

Arachis Oil

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Reichert-Meissl Value.	Hehner Value.	Iodine Value.	Fatty Acids. Melting Point ° C.	Fatty Acids. Solidification Point ° C.	Fatty Acids. Mean Molecular Weight.
0·917–0·9256	185·5–196	0·48	95·5	92–100·8	28·3	25–22	281·8

Arachis oil, which is also known as earthnut or peanut oil, is expressed from the seeds of *Arachis hypogæa*, which is cultivated in the United States, in India and in Africa. The best quality is obtained by cold expression (38 per cent.), whilst the residue yields another 10 per cent. when heated and pressed.

The cold-drawn oil has a flavour of the fresh nuts, and is used for food, more particularly as a cheaper substitute for olive oil. Oil of the second and subsequent pressings is used for lubrication, and in the manufacture of Castille soap.

The best quality, as used for salad oil, is of a pale yellow colour. It solidifies at a much higher temperature than olive oil (*e.g.* 3° to 10° C.), yielding a solid white mass.

Composition.—Arachis oil contains olein, linolin (about 6 per cent. of the unsaturated fatty acids), palmitin, stearin, arachidin and lignocerin. The occurrence of the unsaturated hypogæic acid is doubtful.

Arachis oil is not infrequently used as an adulterant of olive oil. The most trustworthy means of detecting it is by the quantitative estimation of the mixed arachidic and lignoceric acids, which constitute on the average about 4·8 per cent. of the total fatty acids.

The test was devised by Renard,[1] who first fractionated

[1] *Compt. rend.*, lxxiii, 1330.

the lead salts by treatment with ether, and then crystallised the acids recovered from the insoluble lead salts, from hot alcohol.

Archbutt[1] has described a more accurate method of applying the test, and gives a corrected table showing the allowance to be made for the solubility of the mixed arachidic and lignoceric acids in 90 per cent. alcohol. He found that the crystals had a molecular equivalent which corresponded with a mixture of 73·6 per cent. of lignoceric and 26·4 per cent. of arachidic acid, and that they melted at 73·5° C. (highest point observed).

In Bellier's[2] modification of the test, alcohol of 70 per cent. strength is used, and it is possible to detect as little as 5 per cent. of arachis oil in admixture with olive oil.

Tunis olive oil examined in this way yielded a deposit corresponding with 1·5 per cent. of arachis oil, whilst cottonseed oil and sesamé oil gave amounts corresponding with 0·72 per cent. and 0·48 per cent. respectively.

As a rapid means of detecting arachis oil in olive oil Biazzo and Vigdorcik[3] recommend the following modification of a method devised by Kreis and Roth.[4]

The solid fatty acids which have been separated by the lead-ether method are dissolved in 50 c.cm. of 90 per cent. alcohol (containing 10 drops of N/1 hydrochloric acid per litre), the flask immersed in water at 15° C. for 30 minutes, and the crystals which separate dissolved in 25 c.cm. of alcohol, which is cooled as before. If crystals still separate they are dissolved in 12·5 c.cm. of alcohol, the solution again cooled, and any further crystals dissolved in 5 c.cm. of alcohol, which is then allowed to stand at the ordinary temperature. In this way an oil containing 5 per cent. of arachis oil will yield a sufficient amount of crystals for the determination of the melting point, which will be about 73·5 to 74° C.

From a critical examination of Renard's method, Evers[5]

[1] *J. Soc. Chem. Ind.*, 1898, xvii, 1124.
[2] *Ibid.*, 1899.
[3] *Analyst*, 1917, xlii, 85.
[4] *Ibid.*, 1913, xxxviii, 160.
[5] *Ibid.*, 1912, xxxvii, 487.

has found that errors are caused by the solubility of arachidic acid in 70 per cent. alcohol, and suggests the following modification:—Five grms. of the oil are saponified for five minutes, beneath a reflux condenser, with 25 c.cm. of alcoholic potassium hydroxide (80 grms. potassium hydroxide in 80 c.cm. of water, made up to a litre with 90 per cent. (by vol.) alcohol. The hot soap solution is treated with 7·5 c.cm. of dilute acetic acid (1 : 2), and 100 c.cm. of 70 per cent. alcohol containing 1 per cent. (by vol.) of hydrochloric acid. After being cooled for an hour at 12° to 14° C. the liquid is filtered, and the residue washed with the mixture of 70 per cent. alcohol and acid, at 17° to 19° C., until the washings do not become turbid on the addition of water. The residue is then dissolved in hot 90 per cent. alcohol (25 to 70 c.cm.) and cooled to a definite temperature between 15° and 20° C. Any crystals formed are collected after one to three hours, and washed with a definite quantity of 90 per cent. alcohol, and subsequently with 50 c.cm. of 70 per cent. alcohol. They are then dissolved in ether, dried at 100° C. and weighed. If they melt below 71° C. they should be recrystallised from 90 per cent. alcohol. Should only a small amount of crystals (or none) be formed, sufficient water is added to reduce the strength of the alcohol to 70 per cent., and the crystals formed after an hour at 17° to 19° C. are washed with 70 per cent. alcohol, weighed, and recrystallised if melting below 71° C.

The following corrections for the solubility of the acid in 90 per cent. and 70 per cent. alcohol are made:—

Weight of Acids corrected for 90 % Alcohol.	Correction for 100 c.cm., 70 % Alcohol.		
	M. Pt. 71° C.	M. Pt. 72° C.	M. Pt. 73° C.
	grm.	grm.	grm.
Above 0·1 grm.	0·013	0·008	0·006
0·08 to 0·1 grm.	0·011	0·007	0·005
0·05 to 0·08 grm.	0·009	0·007	0·005
0·02 to 0·05 grm.	0·007	0·006	0·005
Less than 0·02 grm.	0·006	0·005	0·004
Factor for conversion of % fatty acids into arachis oil	17	20	22

CANDLE-NUT OIL

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Acetyl Value.	Fatty Acids. Solidification Point ° C.	Fatty Acids. Iodine Value.	Fatty Acids. Iodine Value of Liquid Acids.
0·9254–0·9274	189–195	136–139	9·8	15·5	144	185

Candle-nut oil is expressed or extracted from the kernels of the nuts of *Aleurites moluccana*, which grows in Fiji and other South Sea Islands.

As obtained by expression in the cold it is a pale yellow oil with a pleasant odour and taste, and is used for food purposes.

The hot-pressed oil is used as a medium for paints, though it dries less rapidly than linseed oil, to which it is sometimes added as an adulterant.

The adulteration cannot be readily detected by the insoluble bromide test, since candle-nut oil also yields a considerable deposit with bromine (7·28 to 8·21 per cent.).[1]

COTTON-SEED OIL

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Iodine Value.	Acetyl Value.	Refractive Index at 60° C.	Fatty Acids. Melting Point ° C.	Fatty Acids. Solidification Point ° C.	Fatty Acids. Iodine Value of Liquid Acids.
0·9230–0·926	191–195	108–116	21·1	1·4570	35–40	35–32	137–149

Cotton-seed oil is obtained by expression (or extraction in the case of technical oils) from the seeds of the cotton plant, *Gossypium*, which is cultivated in the United States, Egypt, India and other countries.

The crude oil, separated by the methods described on

[1] Walker and Warburton, *Analyst*, 1902, xxvii, 237.

p. 27, is subsequently refined with alkali (p. 32), which neutralises the free fatty acids, and precipitates a large amount of vegetable impurities. Owing to this treatment, cotton-seed oil is, as a rule, nearly neutral, and has a bland taste.

Composition.—Cotton-seed oil is mainly composed of the glycerides of oleic and linolic acids (about 17 to 18 per cent.), with glycerides of solid fatty acids, chiefly palmitic, with a small amount of stearic acid.

When chilled, it yields a deposit of "stearine," which consists mainly of palmitin with about 4 per cent. of stearin, and glycerides of the liquid fatty acids.

The oil from which the "stearine" has been separated is technically known as "winter oil," since it does not solidify so readily in cold weather.

Colour Reactions.—Cotton-seed oil is one of the few vegetable oils which give distinctive colour reactions. For example, when shaken with an equal volume of strong nitric acid and allowed to stand for 24 hours it gives a brown coloration. This test will detect a small proportion of cotton-seed oil in olive oil.

Bechi's Silver Nitrate Test.[1]—The oil is heated with a mixture of the following solutions—

1. Silver nitrate, 1 grm. in 250 c.cm. of 98 per cent. alcohol; ether, 40 c.cm.; and nitric acid, 0·1 grm.
2. Colza oil, 15 c.cm. in amyl alcohol, 100 c.cm. Ten c.cm. of the oil are shaken with 1 c.cm. of reagent (1) and then with 10 c.cm. of reagent (2), and then divided into two parts, one of which is heated for 15 minutes in boiling water. A red-brown coloration in the heated portion indicates the presence of cotton-seed oil.

Milliau[2] found it preferable to apply the test to the free fatty acids rather than to the oil itself.

Halphen's Test.[3]—Cotton-seed oil contains a constituent

[1] *Zeit. anal. Chem.*, 1894, xxxiii, 560.
[2] *J. Soc. Chem., Ind.*, 1893, xii, 716.
[3] *Ibid.*, 1897, xvi.

which gives an orange-red coloration when the oil is heated with an equal volume of a mixture in equal parts of amyl alcohol and carbon bisulphide (containing about 1 per cent. of free sulphur). The intensity of the coloration varies with the variety and previous treatment of the oil, but the reaction is capable of detecting 5 per cent. or less of cotton-seed oil in admixture with other oils.

As in the case of the silver nitrate test, the substance which reacts with Halphen's reagent is destroyed when the oil is heated to 250° C.

Soltsien[1] found that certain American lards gave a coloration with this test indicating the presence of about 1 per cent. of cotton-seed oil, which was possibly due to the pigs having been fed upon cotton-seed cake. Sjollema and Tulleken[2] also obtained a similar result with the butter from the milk of cows whose fodder had included cotton-seed cake.

Apart from the colour reactions, the presence of cotton-seed oil in olive oil may be detected by the iodine value of the liquid fatty acids, and the melting point of the "stearine" which separates from the oil, whilst the phytosterol test will detect its presence in butter fat and lard.

Cotton-seed oil is extensively used as a salad oil, and is made up into "compound lard" and margarine, either after admixture with solid fats, or, more recently, after hydrogenation (Chap. VIII).

Linseed Oil

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Hehner Value.	Iodine Value.	Refractive Index.	Fatty Acids.		
					Melting Point ° C.	Solidification Point ° C.	Molecular Equivalent.
0·932–0·937	188–193	95	185–195	1·466	21–24	19–20	307

[1] *Chem. Centralbl.*, 1901, i, 539.
[2] *Analyst*, 1902, xxvii, 364.

Linseed oil is obtained from the seeds of the flax plant *inum usitatissimum*), which is extensively cultivated in ussia, India, Egypt, South America and the United States.

Most of the oil is used in the manufacture of paints and irnishes, but it is also a valued edible oil in certain countries, otably Poland and parts of Russia. When intended for od, it is separated by cold expression, for the subsequent ields of oil obtained by hot pressure have a sharp, unpleasant iste, and are, therefore, only fit for industrial purposes.

Composition.—Linseed oil consists of about 10 to 15 per ent. of glycerides of solid fatty acids, mainly palmitin, and 5 to 90 per cent. of the glycerides of liquid fatty acids, which, ccording to Hazura and Grüssner, consist of approximately per cent. of oleic acid, 15 per cent. of linolic acid, 15 per ent. of linolenic acid, and 65 per cent. of isolinolenic acid.

It was found by Hehner and Mitchell[1] that raw linseed oil ielded 24 per cent. or more of an insoluble bromide melting it 143·5° to 144° C. and containing 56·3 per cent. of bromine. This is probably the bromide of a mixed glyceride, oleo-dilinolenin. A test of the purity of linseed oil was based upon the proportion of this bromide yielded by an oil. Boiled oils yield a much smaller proportion of insoluble bromide, whilst their fatty acids yield less hexabromide (*see* p. 50).

The test is conveniently applied by dissolving a weighed quantity of the oil (1 grm.) in a mixture of 40 c.cm. of ether and 5 c.cm. of glacial acetic acid, adding an excess of bromine, and collecting the precipitate, after six hours, on counter-poised filter papers, which are then dried in the water oven.[2]

Properties.—An important characteristic of linseed oil is its pronounced drying property. When exposed to the air in a thin film it is converted into a solid compound, the so-called "linoxyn," the formation of which appears to be due partly to oxidation and partly to polymerisation.

This rapid drying capacity appears to be associated with the high proportion of linolenic and isolinolenic acids in the oil, an indication of which is afforded by the iodine value.

[1] *Analyst*, 1898, xxiii, 317.
[2] Ingle, *J. Soc. Chem. Ind.*, 1911, xxx, 344.

The older recorded iodine values did not, as a rule, exceed about 180 to 185, which was probably due to insufficient time being allowed for the absorption of Hübl's solution.

Later values, obtained by means of Wijs' reagent, are usually about 190, and may exceed 200 (Williams). The iodine values are greatly reduced by the process of "boiling."[1]

The principal substances used to adulterate linseed oil are rosin, cotton-seed oil, rape oil and fish oils.

Their presence is indicated by variations from the usual values of linseed oils, and by special tests, such as the Liebermann-Storch reaction for rosin, Halphen's test for cotton-seed oil, and the formation and separation of behenic acid in rape oil.

The presence of fish oils is indicated by the blackening of the insoluble bromide when heated, and by the cholesteryl acetate test.

Maize Oil

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Reichert-Meissl Value.	Hehner Value.	Refractive Index at 15·5° C.	Fatty Acids.		
					Melting Point ° C.	Solidification Point ° C.	Iodine Value of Liquid Acids.
0·9215–0·9220	189–193	4·2	93–95	1·4768	18–20	19	143

The germs of the maize plant, *Zea mais*, which are obtained as a by-product in the manufacture of maize starch, contain approximately 50 per cent. of oil, about three-quarters of which can be separated by expression.

The freshly-drawn oil is of a golden yellow colour, and has the characteristic odour of the grain. It is used as an edible oil, more especially in the preparation of oleomargarine and artificial lard in the United States, although usually in admixture with cotton-seed oil, since its pronounced odour is liable to be perceptible in the finished product.

It consists, in the main, of glycerides of oleic and linolic

[1] Williams, *Analyst*, 1895, xx, 277.

acids, and of solid fatty acids (palmitic acid), which form about 7 per cent. of the mixed fatty acids. The fairly high Reichert-Meissl value indicates the presence of appreciable amounts of volatile fatty acids. Another characteristic of this oil is its high proportion of unsaponifiable matter (usually 1·5 to 2 per cent. or more), consisting of lecithin and phytosterol (or sitosterol).

With the elaidin test it behaves like cotton-seed oil, forming a semi-solid mass, and its drying capacity is also similar.

Olive Oil

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Hehner Value.	Iodine Value.	Fatty Acids. Melting Point ° C.	Fatty Acids. Solidification Point ° C.	Fatty Acids. Mean Molecular Weight.
0·916–0·919	185–196	94–96	79–93	24–30	21·5–23	279.4

Olive oil is expressed from the fruit of different species of olive, and especially *Olea europœa*, varieties of which are cultivated in Italy, France, Spain, Tunis and other Mediterranean countries.

The best quality of oil is obtained from the freshly picked olives, which are gently crushed between cloths, and yield the so-called virgin oil.

Another good quality is expressed by rollers from the ripe fruit, without crushing the stones, whilst a third quality is obtained by crushing the *marcs* and stones, and expressing them with boiling water. Finally, the residue is extracted with carbon bisulphide, to obtain an industrial oil.

The flavour of the different products varies considerably with the freshness of the fruit and the method of expression. In the lower grades of oil, which are extracted by heavy pressure in the presence of boiling water, other constituents of the fruit are also extracted, and influence the flavour. If the fruit was not freshly picked, or is damaged, hydrolysis of the oil, with the liberation of free fatty acids, will take

place, and the expressed oil will show a high acid value, and have an unpleasant acrid taste.

The most valued commercial grades of olive oil are those produced in Tuscany (Lucca oil) and in Provence, whilst good qualities are derived from Spain and Portugal. Tunisian and Algerian oils are not regarded as equal to the French and Italian oils in flavour.

A considerable quantity of olive oil is now produced in California, whilst Australia and South Africa also produce oil, although mainly for local consumption.

Composition.—Olive oil consists of about 75 per cent. of glycerides of liquid fatty acids, mainly oleic acid, with a small proportion of linolic acid. The solid fatty acids consist chiefly of palmitin. It is owing to the presence of these solid glycerides that olive oil becomes turbid in cold weather.

The free fatty acids usually range from about 0·3 per cent. (as oleic acid) to about 1 or 2 per cent. in the case of the best qualities of oil, but in oil of the second and third quality it may be from 5 to 8 per cent., and in industrial oils as much as 25 per cent.

The iodine value is generally 80 to 83, but in the case of oil from certain countries may be much higher. Thus values of 79 to 88 have been recorded for Italian oils,[1] and 93·67 for a specimen of Indian oil.

Adulterants.—The presence of rape oil in olive oil may be detected by separating the erucic acid, which is a characteristic unsaturated fatty acid of rape oil, by the lead-ether method, and hydrogenating the ethereal solution in the presence of palladium. The hydrogenated fatty acids are then fractionally crystallised from alcohol, and the melting point of the last fraction determined. If behenic acid, formed by the hydrogenation of the erucic acid be present, they will show a melting point above 71° C., the usual figure being above 76° C.

The details of the process have been worked out by Biazzo and Vigdorcik.[2]

[1] *J. Soc. Chem. Ind.*, 1892, xi, 848.
[2] *Analyst*, 1917, xlii, 86.

Cotton-seed oil may be detected by Halphen's test, sesamé oil by the Baudouin reaction, and arachis oil by estimation of the arachidic acid.

Poppy Oil

Typical Values

Specific Gravity at 15° C.	Saponification Value.	Hehner Value.	Iodine Value.	Fatty Acids.		
				Melting Point ° C.	Solidification Point ° C.	Iodine Value of Liquid Acids.
0·924–0·926	193–195	95·4	131–141	20·5	17–19	151·7

Poppy oil is derived from the seeds of the poppy, *Papaver somniferum*, which yield upwards of 50 per cent. on expression. The plant is grown for this purpose in Egypt, Asia Minor, Persia and India, and, to a less extent, in some other countries.

The oil obtained in the first pressing, without the application of heat, is nearly colourless, and has a pleasant aroma and flavour. Hence, it is in common use as a salad oil, and is also used as an adulterant of olive oil.

The oil obtained by hot expression is used as a medium for oil paints, its pale colour rendering it particularly suitable for the more delicate pigments. It dries somewhat less rapidly than linseed oil.

It contains about 7 per cent. of solid fatty acids, whilst, according to Hazura and Grüssner, the liquid fatty acids consist of approximately 30 per cent. of oleic acid, 65 per cent. of linolic acid, and 5 per cent. of linolenic acid. Unlike linseed oil, it yields no insoluble bromide (Hehner and Mitchell).

Sesamé Oil

Typical Values

Specific Gravity.	Saponification Value.	Reichert-Meissl Value.	Iodine Value.	Refractive Index.	Fatty Acids.	
					Melting Point ° C.	Solid Point ° C.
0·9210–0·9237	188–193	1·2	103–108	1·4568 at 20° C	24–26	20–22

Sesamé oil is expressed from the seeds of *Sesamum orientale*, which is cultivated in the tropics, South Africa and the United States.

It is a pale yellow oil with a pleasant odour and taste.

It consists, in the main, of the glycerides of oleic and linolic acid, with smaller quantities of the glycerides of solid fatty acids, including stearin, palmitin and myristin. The unsaponifiable matter (1 to 1·4 per cent.) consists of a phytosterol, a crystalline dextrorotatory substance, *sesamin*, and a substance termed *sesamol*, which reacts with furfural and hydrochloric acid.

The Baudouin Test.—This depends on the presence of the phenoloid substance *sesamol*, which gives a red coloration when the oil is shaken with cold hydrochloric acid and cane sugar. This coloration was found by Villavecchia and Fabris,[1] to be due to the formation of furfural by the action of the hydrochloric acid on the sugar, and they recommended the use of an alcoholic solution of furfural mixed with hydrochloric acid in place of Baudouin's original reagent.

The test is capable of detecting as little as 1 per cent. of sesamé oil in admixture with other oils, but it has been found that certain varieties of olive oil are liable to give a similar coloration. To obviate this source of error the test should be applied to the mixed fatty acids from the oil.

Bishop's Reaction.[2]—On shaking sesamé oil which has been exposed to air and light with 1½ times its volume of hydrochloric acid, a green coloration is imparted to the acid layer. This was attributed by Kreis to the presence of oxidation products of the glycerin, and the test may be used as a means of detecting rancidity in other fats. Thus, old lard or butter, which do not give any coloration in the test, colour the acid green when mixed with fresh sesamé oil.

Sesamé oil is a typical semi-drying oil, as might be anticipated from its iodine value. In the elaidin test it yields a reddish-brown butter-like mass after standing for 24 hours.

The presence of cotton-seed oil in sesamé oil could be

[1] *J. Soc. Chem. Ind.*, 1894, xiii, 69.
[2] *Ibid.*, 1890, ix, 112.

detected by Halphen's test (*q.v.*), whilst arachis oil would be found by the separation and estimation of arachidic acid.

The addition of a certain proportion of sesamé oil to margarine is obligatory in certain countries, including Germany and Austria.

Sunflower Oil

Typical Values

Specific Gravity at 15 °C.	Saponification Value.	Iodine Value.	Fatty Acids.			
			Melting Point °C.	Solidification Point.	Neutralisation Value.	Iodine Value of Liquid Acids.
0·924–0·926	189–193	129–133	22–24	19·8	201·5	154·3

Sunflower oil is derived from the seeds of the sunflower, *Helianthus annuus*, which is cultivated on a very extensive scale in Russia. The seeds are steam-heated, crushed to a paste and expressed, and yield a pale yellow oil, which is in great demand for cooking purposes and as a salad oil. According to Jean, 100 kilos. of seeds yield from 15 to 20 kilos. of edible oil when expressed without heat.

Sunflower oil dries more slowly than linseed or poppy oils, but eventually yields a hard film. It consists of glycerides of oleic, linolic and palmitic acids, with probably some linolenic acid.

Walnut Oil (Nut Oil)

Typical Values

Specific Gravity at 15 °C.	Saponification Value.	Hehner Value.	Iodine Value.	Refractive Index.	Fatty Acids.		
					Melting Point °C.	Solidification Point °C.	Iodine Value of Liquid Acids.
0 9250–0·9268	192–197	94–95·5	142–146	1·4689	15–20	14·3–16	167

The kernels of the walnut tree (*Juglans regia*) contain about 65 per cent. of oil, which may be separ^ted by expression.

The cold-drawn oil is used in some parts of Europe as an edible oil, and, when fresh, has a pleasant taste. Oil of the second expression, however, obtained with the aid of heat, has an acrid taste and is only suitable for technical purposes.

Composition.—The solid fatty acids contain myristic and lauric acids, whilst the liquid fatty acids were found by Hazura and Grüssner to consist approximately of oleic acid, 7 per cent.; linolic acid, 80 per cent.; and linolenic and isolinolenic acids, 13 per cent.

Walnut oil yields from 1·5 to 1·9 per cent. of an insoluble bromide containing 58·58 per cent. of bromine (Hehner and Mitchell). Apparently this is the bromide of a mixed glyceride similar to that given by linseed oil.

Properties.—The oil obtained by cold expression is of a pale yellow tint, whilst that yielded by hot expression is much darker in colour.

It dries readily, forming a transparent film; and although it is not so rapid a drier as linseed oil, its light colour makes it a more suitable medium for white paints.

The presence of linseed oil in walnut oil may be detected, and its amount approximately estimated by Hehner and Mitchell's insoluble bromide test,[1] the calculation being based upon a yield of 24 per cent., which is about the usual proportion given by pure linseed oil (*see* p. 64).

Other adulterants of walnut oil are sesamé and arachis oils and resin oil.

[1] *Analyst*, 1898, xxiii, 316.

CHAPTER VI

CHARACTERISTICS OF INDIVIDUAL EDIBLE FATS

Bassia Tallow

Typical Values

Fat from	Specific Gravity at 99°/15° C.	Refractive index (Zeiss) at 40° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Free Fatty Acids, as Oleic Acid. Per Cent.	Unsaponifiable Matter. Per Cent.
Bassia latifolia	0·8595	47·7	192·2	59·4	—	24·6	—
B. longifolia .	0·8624	49·3	189·8	62·6	—	3·3	—
B. butyracea .	—	47·8	188·2	42·6	1·31	8·74	1·36

As will be seen by the figures quoted above from analyses by Revis and Bolton,[1] there is a close chemical similarity in the fats derived from various species of *Bassia*.

In commerce the seeds of *B. latifolia* and of *B. longifolia* are frequently mixed, and the fats are known not only as *Bassia tallow*, but also as "Mohrah" or "Illipé" butter.

B. longifolia grows in Southern India, whilst *B. latifolia* is found in Central India, but not in the South. Its seeds are rounder and not so long as those of the other species. The seeds of *B. butyracea*, which is also an Indian species, are smaller than those of either of the other plants. The fat is termed "Phulwa" by the natives.

The freshly expressed fat from the seeds of these plants is of a pale yellow colour. It is used as food in India, and, if properly refined, can be used as a substitute for lard.

[1] *Allen's Commercial Organic Analysis*, ix, p. 147.

The fat from the seeds of another species, *B. Mottleyana*, was examined by Brooks. As prepared by the Dyaks for food it is a pale yellow oil, with analytical characteristics very similar to those of the other species of *Bassia*. It has not yet become a commercial product.[1]

BEEF FAT (BEEF TALLOW)

Typical Values

Specific Gravity.	Melting Point ° C.	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Fatty Acids.			
						Melting Point ° C.	Solidification Point ° C.	Neutralisation Value.	Iodine Value of Liquid Acids.
0·952 at 15° C. 0·860 at 100° C.	43–48	194–198	95·5–96	0·25	38–44	43–47	43–45	197–201	92·4

The fat from oxen and cows is commercially known as *beef tallow*, and is principally used in the manufacture of soap and candles.

A large proportion, however, of the specially selected fat, mainly from the kidneys, is used for the preparation of oleomargarine.

This fat is cleaned and hardened by artificial cold, and then shredded and crushed by machinery, and heated in steam-jacketed vessels at a temperature of 40° to 45° C.

The fat which separates from the tissue at this temperature is known as "premier jus." It is left to cool in shallow vessels until most of the "stearine" crystallises from it, and is then pressed in a hydraulic press.

The more liquid portion which is expressed forms the "oleo oil" or "oleomargarine" which is used in the manufacture of margarine, whilst the residue in the press consists of "beef stearine."

[1] *Analyst*, 1909, xxxiv, 207.

Beef fat varies greatly in consistence and composition with the food of the animal and the part whence the fat was derived. This is shown, for example, by the following melting points obtained by Mayer[1] with the fat from different parts of the body of an ox:—Intestines, 50·0° C.; lungs, 49·3° C.; caul, 49·6° C.; heart, 49·5° C.; neck, 47·1° C.; and groins, 42·5° C.

This variation in the melting points depends upon the relative proportions of solid and liquid glycerides in the fats.

Various mixed glycerides have been separated from beef fat, including oleodipalmitin, stearodipalmitin, oleopalmito-stearin and palmitodistearin.

The presence of distinctive glycerides in beef fat and in lard affords an explanation of the different forms of the crystals which separate from a solution of the fats in ether (*see* p. 6).

A sample of beef "stearine" examined by Hehner and Mitchell[2] had an iodine value of 2·0, and was therefore practically free from olein. The mixed fatty acids contained 51 per cent. of stearic acid.

According to Farnsteiner,[3] beef fat contains a small proportion of linolenic acid.

Borneo Tallow

This fat is obtained from the seeds of a number of plants, of which the best known is *Shorea stenoptera*, which grows in North-West Borneo.

The seeds are imported into England, under the name of "Pontianak illipé nuts," and yield a hard and greenish fat, which on keeping becomes yellow or white. It has a granular structure, and a pleasant odour.

Owing to these characteristics Borneo tallow is used as a substitute for cacao butter, under the commercial name of "green butter." It melts at about 40° to 45° C.

[1] Wagner's *Jahresber.* 1880, 844.
[2] *Analyst*, 1896, xxi, 319.
[3] *Zeitsch. Nahr. Genussm.*, 1899, 25.

To distinguish between this fat and cacao butter, Revis and Bolton[1] use the following modification of Halphen's test:—One grm. of the filtered fat is dissolved in 2 c.cm. of a mixture of carbon tetrachloride and petroleum spirit (1 : 1), and 2 c.cm. of the solution are transferred to a test tube 6 in. by ½ in. in diameter, which is cooled in water. A solution of bromine in an equal volume of carbon tetrachloride is then added, drop by drop, with constant shaking, until the colour of the bromine persists. The tube is then closed and allowed to stand, and if, after fifteen minutes, the solution remains clear, cacao butter is either absent or not present to the extent of more than 10 per cent. A turbidity indicates the probable presence of cacao butter. A similar turbidity, however, is given by the fat from the seeds of a species of *Gutta*, but is flocculent in form, whereas the turbidity due to cacao butter is non-flocculent.

CACAO BUTTER

Typical Values

Specific Gravity at 15° C.	Melting Point ° C.	Solidification Point ° C.	Saponification Value.	Hehner Value.	Reichert-Meissl Value.	Refractive Index at 60° C.	Fatty Acids.			
							Melting Point ° C.	Solidification Point ° C.	Neutralisation Value.	Iodine Value.
0·964–0·976	28–34	21·5-26	192–198	94·6	0·3–0·8	1·4496	48–53	47–49	190	33–39

Cacao butter is present to the extent of about 40 to 50 per cent. in the beans of the cacao tree, *Theobroma cacao*.

To separate the fat, the beans are roasted and expressed with the aid of heat. As it is usual to add a proportion of an alkali, prior to the expression, the commercial fat is generally neutral.

It is moulded into slabs, which are brittle, of a pale yellow colour, and have a pronounced odour of the bean.

Composition.—Cacao butter consists of the glycerides of fatty acids composed of about 60 per cent. of solid fatty acids

[1] *Analyst*, 1913, xxxviii, 201.

including palmitic, stearic and arachidic acid, and about 40 per cent. of liquid fatty acids, mainly oleic acid, with about 7 per cent. of linolic acid.

Mixed glycerides have been isolated from the fat, such as oleopalmitodistearin by Klimont and oleodistearin by Fritzweiler.

The proportion of stearic acid in the mixed fatty acids is about 40 cent. (Hehner and Mitchell).

Owing to its mode of preparation, cacao butter usually has a very low acid value (1 to 2), and this characteristic and the high melting point prevent the fat from becoming rancid as readily as softer fats such as coconut oil.

Cacao butter is extensively used in the preparation of chocolate creams, but is liable to be adulterated with cheaper fats such as coconut and palm-kernel oil "stearines."

The presence of these fats will lower the melting point of the fat and fatty acids, raise the saponification value and the Reichert-Meissl value, and lower the iodine value.

Estimation of the amount of stearic acid in the mixed fatty acids by the method of Hehner and Mitchell will also afford evidence of the adulteration.

For the detection of animal fats, such as beef and mutton tallow, in cacao butter, the cholesteryl acetate test is the most trustworthy method.

Coconut Oil

Typical Values

Specific Gravity.	Saponification Value.	Hehner Value.	Reichert-Meissl Value.	Polenske Value.	Iodine Value.	Melting Point ° C.	Fatty Acids. Melting Point ° C.	Fatty Acids. Solidification Point ° C.	Fatty Acids. Mean Molec. Equivalent.
0·9030 at 100 ° C.	255–260	88·6–90·5	6·7–7·5	16·8	8·2–9·5	23–25	24–27	21–25	196–204

Coconut oil is expressed from the kernels of the nuts of the cocoa palm (*Cocos nucifera* and *C. butyracea*), large quantities of which are dried and exported in the form of "copra."

When freshly expressed the fat is a white semi-solid mass, which contains only a small proportion of free fatty acids, but commercial samples usually contain about 5 per cent. or more, and in some cases as much as 25 per cent. has been recorded.

It has the characteristic odour of the coconut, which becomes intensified on keeping. This odour can be removed by special treatment (*see* p. 35), but is liable to recur. The fat also turns rancid much more readily than more solid fats such as cacao butter.

The methods in use for deodorising coconut oil and removing rancidity are described on p. 33.

It is used in the manufacture of substitutes for butter and lard (nut butters), and as a substitute for cacao butter.

The more solid portion "stearine" separated by pressure at a suitable temperature (p. 29) is more suitable for such purposes than the oil itself.

Inferior and acid products are used in the manufacture of "salt water" soap, night-lights, etc.

Composition.—Coconut oil is composed of the glycerides of volatile and non-volatile fatty acids, about 60 per cent. of which consist of lauric and myristic acids.

By the method of alcoholysis of Hanùs and Thian[1] it is possible to separate by distillation the fatty acids in the form of ethyl or methyl esters, so as to obtain an approximate estimation of their quantity. In this way Elsdon[2] found a specimen of the fat to contain glycerides of the following fatty acids: Caproic, 2; caprylic, 9; capric, 10; lauric, 45; myristic, 20; palmitic, 7; stearic, 5, and oleic acid, 2 per cent.

Owing to the presence of these considerable quantities of volatile fatty acids, coconut oil has a fairly high Reichert-Meissl value, and this increases the difficulty of estimating the quantity of margarine in an adulterated butter. To overcome this difficulty, Polenske devised a method of estimating a proportion of the volatile insoluble fatty acids (p. 47), whilst Shrewsbury and Knapp based a method upon

[1] *Analyst*, 1907, xxxii, 89; 1908, xxxiii, 281.
[2] *Ibid.*, 1913, xxxviii, 8,

the large proportion of lauric and myristic acids in the fat (*see* Chap. VII).

A sample of a hard coconut "stearine" intended as a substitute for cacao butter had the following characters[1]: Specific gravity at 100° C., 0·8700; melting point, 29·5° C.; solidifying point, 26·5; saponification value, 252; iodine value, 4·5; Reichert-Meissl value, 3·4. *Fatty acids:* melting point, 28·1° C.; solidification point, 27·4° C.; and mean molecular weight, 209.

Goose Fat

Typical Values

Fat of	Specific Gravity at 15 °C.	Melting Point °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Fatty Acids. Melting Point °C.	Solidification Point °C.	Neutralisation Value.	Iodine Value.
Domestic goose	0·9274	32–34	193	67·6	0·3	95·3	38–40	31–32	202·4	65·3
Wild goose	—	—	196	99·6	—	—	34–40	33–34	196·4	65·1

The fat of the goose is a semi-solid yellow butter-like mass, having a distinctive odour.

It contains glycerides of oleic, palmitic and stearic acids, together with a small proportion of those of volatile fatty acids.

As in many other cases where the fat of wild and domesticated animals or birds has been examined, the fat of the wild goose has a decidedly higher iodine value than that of the bird in captivity, and, judging by the low iodine value of the fatty acids, this acid would appear to be readily oxidisable. This points to the presence of a more unsaturated fatty acid than oleic acid in the fat of the wild bird. It is interesting to note that the fat of a wild goose which had been kept for two years in captivity, showed an iodine value very similar to that of the fat of the ordinary goose (67·6).[2]

Polenske has devised a method of recognising goose fat (p. 82).

[1] Sachs, *Analyst*, 1908, xxxiii, 123.
[2] Amthor and Zink, *Zeitsch. anal. Chem.*, 1897, xxxvi, 9.

HARE FAT

Typical Values

Specific Gravity at 15° C.	Melting Point ° C.	Saponification Value.	Iodine Value.	Reichert Value.	Hehner Value.	Fatty Acids. Melting Point ° C.	Solidification Point. ° C.	Neutralisation Point ° C.	Hehner Value.
0·9349	35–40	200·9	102·2	1·59	95·2	44–47	36–40	209·0	93·3

The fat of the hare varies in colour from pale yellow to deep orange, and is similar to horse fat in appearance and consistence. It resembles the fat of the wild rabbit in drying rapidly when exposed to the air, and this characteristic and its high iodine value points to the presence of the glycerides of fatty acids more unsaturated than oleic acid (linolic and, probably, linolenic acids).

The ready oxidisability of the fat would also account for its speedily becoming rancid when kept.

When allowed to stand it separates into a yellow oil and a white crystalline deposit.

HORSE FAT

Typical Values

Specific Gravity at 15° C.	Melting Point ° C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Fatty Acids. Melting Point ° C.	Solidification Point.	Neutralisation Value.	Iodine Value.
0·9189	39	196·8	73–86	2·14	96–97·8	37·5–9·	37·3	202·6	83·9–87·1

Horse fat is a soft yellow fat with a characteristic unpleasant odour.

It yields a crystalline deposit ("stearine") when allowed to stand.

The fat varies in consistence with the part of the animal from which it was derived, but is never as firm as even a soft lard.

In countries where horse-flesh forms part of the staple food, the fat is also used in place of more expensive oils.

It contains glycerides of oleic and linolic acids (Farnsteiner), and of solid fatty acids, mainly palmitic acid. Hehner and Mitchell were unable to detect any stearic acid in a sample of kidney fat by their method of crystallisation from alcohol saturated with pure stearic acid (p. 52).

LARD

Typical Values

Specific Gravity.	Saponification Value.	Hehner Value.	Iodine Value.	Melting Point °C.	Fatty Acids.			
					Melting Point °C.	Solidification Point °C.	Molecular Equivalent.	Iodine Value of Liquid Acids.
0·860 at 100 °C.	195–200	93–95	50–66	30–45	37–46	39–42	278	94–96

The method of rendering lard from the fat from different parts of the pig, and a description of the different grades, were given on p. 31.

Composition.—The composition of the fat of the pig varies with the variety of the breed, the food of the animal, and the part whence it was taken.

The glycerides of stearic, palmitic, myristic, lauric, oleic and linolic acids have been identified, whilst traces of linolenic acid were found by Farnsteiner.[1]

The amounts of stearic acid estimated by Hehner and Mitchell[2] in fat from different parts were as follows: head, 9; ham, 8·8; breast, 11·5; flare, 15; and back, 8·8 per cent.

In the case of commercial lard the mixed fatty acids contained from 6 to 16 per cent. of stearic acid.

It is probable that the high iodine value of American lards (upwards of 68 in some cases) is due to the presence of a greater proportion of linolic and linolenic acids.

[1] *Zeitsch. Nahr. Genussm.*, 1899, ii, 1.
[2] *Analyst*, 1896, xxi, 326.

It is interesting to note that the iodine value of the fat of the wild boar is still higher than that of the fat from American pigs.

When lard is crystallised from ether it yields characteristic crystals with chisel-shaped ends, whereas beef and mutton fat give needle-shaped crystals in fan-like groups.[1] This has been shown by Kreis and Hafner to be due to the presence of distinctive glycerides, and a method of detecting beef and mutton fat in lard has been based upon this difference (*infra*).

Freshly prepared lard contains a very small proportion of free fatty acids (usually below 0·5 per cent.), and generally less than 0·5 per cent. of water.

Tests of Purity.—Lard is liable to be adulterated with beef and mutton fat, with vegetable fats, such as coconut and palm-kernel oils, and with vegetable oils, such as cotton-seed, maize and sesamé oils.

The presence of vegetable oils may be detected by the phytosteryl-acetate test (p. 53), whilst cotton-seed and sesamé oils have characteristic colour reactions, and will increase the iodine value. It has been found, however, that the lard of pigs fed upon cotton-seed cake will show Halphen's reaction for cotton-seed oil.[2] Coconut oil and palm-kernel oils contain a considerable proportion of volatile fatty acids, and their presence in lard may therefore be detected by the Reichert-Meissl and Polenske values. Hanùs and Thian[3] found that the nature of ethyl esters yielded by a lard gave trustworthy information of the presence of coconut oil.

Detection of Animal Fats.—Considerable importance was at one time attached to Belfield's crystallisation test (*loc. cit.*), and Stock[4] attempted to make it quantitative by weighing the deposits and comparing the results with those obtained under definite conditions from pure lard and lard adulterated with various proportions of beef stearine. Dunlop,[5] however, found that by continued recrystallisation of the feather-like

[1] Belfield, *Analyst*, 1888, xiii. 70. [2] See p. 63.
[3] *Analyst*, 1907, xxxii, 89; 1908, xxxiii, 281.
[4] *Ibid.*, 1894, xix, 2.
[5] Dunlop, *J. Soc. Chem. Ind.*, 1906, xxv, 459.

crystals from beef fat, they were at length converted into flat crystals resembling those given by lard.

The test must therefore be used with caution, and only regarded as additional proof of adulteration when the presence of a vegetable oil has been detected.[1]

Polenske's Method.—Polenske's method of detecting certain animal fats in the presence of one another is based upon the fact that the difference between the melting and solidification points ("difference value") is fairly constant for the same kind of fat, but shows pronounced differences in the case of some other kinds of fat.[2]

In making the determination, the clear filtered fat is dried at 102° to 103° C. in a current of dried carbon dioxide, and is then introduced into a U-shaped capillary tube, which is left in contact with ice for 24 hours. The tubes are now attached to a standard thermometer, which is gradually heated in a mixture of water and glycerin from 20° C., first at the rate of 2° C. per minute until within 5° of the melting point, and then at 0·75° C. per minute. The temperature at which the fat becomes perfectly clear is taken as the melting point.

For determining the solidification point, a flat-bottomed tube, containing a column of the fat, 17 cm. high and 1·8 cm. diameter, is surrounded by another tube, to form an air-chamber, and this is immersed in a water-bath. The melted fat is mechanically stirred by a rotating nickel agitator, and the solidification point is taken as the point at which two black marks on the wall of the tube become invisible. Duplicate determinations should agree within 0·2° C.

In the case of beef fat, the difference-values were found by Polenske to range from 12·8 to 14·7, whilst lard showed differences of 19 to 21; and he therefore concluded that all lards showing difference below 18·5 must be regarded as adulterated.

Pure goose-fat had a difference value not exceeding 17, whilst butter-fat showed differences ranging from 11·8 to 14·3.

1 Hehner, *Analyst*, 1902, xxvii, 24.

2 *Arbeit. Kaiserl. Gesundh.-Amt.*, 1907, xxvi, 444; *Analyst*, 1907, xxxii, 382; 1908, xxxiii, 476.

He further concluded that butter-fat was adulterated if it showed a difference value exceeding 14·6, or exceeding 15, after admixture with 25 per cent. of a standard beef tallow (melting at 49° to 49·7° C. and having a difference value of 14·4 to 14·6). But after further experience[1] he regarded only the second test, in admixture with the beef fat, as conclusive, and then only when the difference value of the mixture was both higher than 15, and higher than the value of the butter fat itself.

Bömer and Limprich[2] have shown that the "difference values" depend, in the main, upon the difference in the nature of the glycerides contained in the different fats (*see* p. 6). The α-palmitodistearin of lard shows a difference value of 18·4, whereas the β-palmitodistearin of beef and mutton fat has a difference value of 11·8. The stearodipalmitins from mutton fat and lard give practically identical results (12·2 and 12·4), but it has not been determined whether the two glycerides are identical or are isomeric modifications. The most insoluble glyceride of mutton and beef fats, tristearin, has a difference value of 19·7; but its proportion in beef fat (1 to 2 per cent.) is insufficient to outweigh the effect of the greater proportion of α-palmitodistearin in lard. The relatively higher difference value of mutton fat (16·9) is probably due to the greater proportion of tristearin in that fat (about 3 per cent.).

In Bömer's experience the test is capable of detecting about 20 per cent. of beef fat, and 15 per cent. of mutton fat in admixture with lard, but it is essential that sufficient time should be allowed for the stable form of the glyceride to solidify before applying the test.

The removal from the fat of glycerides containing oleic acid does not materially increase the sensitiveness of the test.

[1] *Arb. Kaiserl. Gesundh.-Amt.*, 1908, xxix, 272.
[2] *Zeitsch. Nahr. Genussm.*, 1913, xxv, 367.

Mutton Fat (Mutton Tallow)

Typical Values

Specific Gravity.	Melting Point °C.	Saponification Value.	Hehner Value.	Iodine Value.	Fatty Acids.			
					Melting Point ° C.	Solidification Point ° C.	Neutralisation Value.	Iodine Value of Liquid Acids.
0·937–0·953 at 15 ° C. 0·858 at 100 ° C.	44–49	192–195	95·5	35–46	49–53	43–46	210	92·7

The more solid portions of the fat of the sheep, which form the commercial *mutton tallow*, resemble beef tallow in general characteristics, but are usually harder, and have a more pronounced odour.

Although mutton fat is sometimes used in the manufacture of margarine, it is much less suitable for the purpose than beef fat.

The variations in the consistence and composition of the fat from different parts of the same animal are greater than in the case of beef fat.

For example, Hehner and Mitchell[1] obtained the following results with the fat taken from different parts of a Scotch sheep eighteen months old—

Fat from—	Iodine Value.	Melting Point of Fatty Acids ° C.	Stearic Acid in Fatty Acids, per cent.
Kidneys	48·16	45·6	26·2–27·7
Back	61·3	41·4	24·8
Neck	48·6	42·2	16·4
Breast	58·2	33·8	About 1
Ham	50·6	40·8	None

The hardest fat (from the kidneys) thus contained the largest proportion of stearic acid and the smallest proportion of liquid fatty acids, whilst the softest fat (that from the

[1] *Analyst*, 1896, xxi, 327.

breast) contained hardly any stearic acid, but a high percentage of liquid fatty acids.

In commerce, the "tallow" used for the manufacture of candles and soap frequently consists of a mixture of beef and mutton tallows, whilst the tallow from the goat is usually sold as "mutton tallow."

Palm Oil

Typical Values

Specific Gravity	Saponification Value.	Hehner Value.	Reichert Value.	Iodine Value.	Fatty Acids. Melting Point ° C.	Solidification Point ° C.	Molecular Equivalent.
0 945 at 15° C. 0·856 at 98/15·5° C.	202	95·6	0·5	51–52	50	43–45	270

The palm oil of commerce is mainly derived from the fruit pulp of the palms *Elæis guineensis* and *E. melanocca*, the former growing in West Africa, and the latter in South America. Many other kinds of palms, however, are now being utilised, more especially in Brazil and other South American countries (*see* p. 87).

The best qualities of the fat are obtained by expressing the fresh fruit, whilst an inferior grade is procured by leaving the fruit to ferment in holes in the ground, and collecting the fat as it separates.

The colour of the fat varies with the mode of preparation from bright orange to dirty brown.

The fresh oil is of the consistence of butter, and is used as an edible fat by the natives of Africa, and in America is employed to colour margarine. The harder fat obtained by the fermentation process is acid and rancid, and only suitable for technical purposes.

It contains palmitin, free palmitic acid, olein and a small quantity of linolin and stearin.

Palm-kernel Oil

Typical Values

Specific Gravity.	Saponification Value.	Hehner Value.	Reichert-Meissl Value.	Polenske Value.	Iodine Value.	Fatty Acids. Melting Point ° C.	Fatty Acids. Solidification Point ° C.	Fatty Acids. Molecular Equivalent.
0·952 at 15° C. 0·8731 at 99/15°C.	245–255	91·5	5–6·8	11·50	10·3–17·5	25–28·5	20–25·5	211

Palm-kernel or palm-nut oil is expressed from the seed-kernels of the fruit of the palm trees, the pulp of which yields palm oil.

It is a white or yellowish fat with a distinctive odour, and differs materially both in properties and composition from palm oil.

Composition.—It closely resembles coconut oil in its general composition, but contains a somewhat lower proportion of the glycerides of the lower fatty acids, as is indicated by its lower Reichert-Meissl and Polenske values.

Elsdon[1] separated the constituents of a sample of palm-nut oil by the method of "alcoholysis" and distillation of the methyl esters, and obtained the following approximate percentage results for this fat and for coconut oil—

	Caproic Acid.	Caprylic Acid.	Capric Acid.	Lauric Acid.	Myristic Acid.	Palmitic Acid.	Stearic Acid.	Oleic Acid.
Palm-kernel oil	2	5	6	55	12	9	7	4
Coconut oil	2	9	10	45	20	7	5	2

These results show that it will not be an easy matter to devise a test which will distinguish with certainty between these fats when in admixture with other fats.

Both are used in the preparation of margarine, and the

[1] *Analyst*, 1914, xxxix, 78.

methods of detecting them in admixture with butter fat are described in Chapter VII.

Brazilian Palm Oils and Palm-kernel Oils.—In addition to the ordinary palm and palm-kernels oils from *Elæis guineensis*, there are numerous palms the fruit of which produces fats of similar character, some of which are already extensively used as edible fats, whilst others will probably be used for this purpose in the near future. Some of the more important of these, of Brazilian origin, have been described by Bolton and Hewer,[1] who give the following details of their characteristics—

1. *Elæis guineensis.*—The fats from the pulp and kernel are suitable for the same purposes as the ordinary African products, but differ considerably therefrom in analytical values.
2. *Astrocaryum vulgare* produces a pulp oil of pale straw colour, and of butter-like consistence. If prepared from fresh fruit containing less than 10 per cent. of free fatty acids, it would be suitable for margarine.
3. *Astrocaryum species.*—The kernel oil would be suitable as a substitute for cacao butter and coconut "stearine."
4. *Acrocomia sclerocarpa*, which grows in large forests in Paraguay, yields a pulp oil resembling palm oil, but of less value. The kernel oil would be suitable for margarine.
5. *Maximiliana regia* (Anajá or kokerite palm) yields an odourless, firm, white, edible fat.
6. *Cocos syagrus* occurs in two distinct types, the fruit kernels of which, however, produce very similar fats.
7. *Attalea funifera* produces kernels with excessively hard shells. They yield a fat similar to, but softer than, coconut oil, and suitable for margarine.
8. *Œnocarpus batava.*—The oil from the pulp of this fruit closely resembles olive oil in its characters, and is particularly suitable for use as a salad oil.

[1] *Analyst*, 1917, xlii, 35.

The following results were obtained with specimens of these fats—

Palm Oils.	Melting Point.		Solidification Point.	Saponification Point.	Refractive Index (Zeiss at 40° C).	Iodine Value.	Free Fatty Acids as Lauric Acid in Kernel, and Oleic Acid in Pulp Oil.	Unsaponifiable Matter.
	Beginning.	Complete						
	° C.	° C.	° C.				Per Cent.	Per Cent.
1. Pulp .	22–24·0	30–30·5	21·9	197·1	48·5–51·5	78·1–88·3	29·8–20·5	—
Kernel	28·5–28·0	30·2–31·0	27·3–27·8	231·4–220–2	40·5–42·7	25·5–31·6	0·55–0·33	—
2. Pulp .	27·0	35·0	—	220·2	52·5	46·4	43·8	0·75
Kernel	29·4–30·0	30·6–32·5	28·6	240–245·2	36·3–37·5	12·2–13·9	0·54–1·65	—
3. Kernel	33	34	32·5	237·0	36·8	12·4	0·36	—
4. Pulp .	—	—	24·9	189·8	40·5	77·2	55·8	—
Kernel	21	22–25·8	19·4–24·9	237–246	37·2–40·1	16–30	0·4–4·7	—
5. Kernel	26	28·5	—	240·9	38·3	16·56	0·33	—
6. Blunt fruit, kernel	23	29	26·8	252·5	37·4	12·5	3·2	—
Pointed fruit, kernel	23	28·7	—	—	36·2	13·4	2·97	—
7. Kernel	22·2	26·1	22·7	246·9	37·1	16·3	2·80	—
8. Pulp .	—	—	7·0	191·8	52·5	78·2	0·48	1·1

The extending use of fats such as these enormously increases the difficulty of the chemist who has to decide upon the composition of a given mixture. In fact, in the case of fats of this type it is even now only possible to express an opinion in general terms as to their probable origin.

Rabbit's Fat

Typical Values

Fat of—	Specific Gravity at 15.	Melting Point °C.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Hehner Value.	Fatty Acids.			
							Melting Point °C.	Solidification Point °C.	Neutralisation Value.	Iodine Value.
Wild Rabbit	0·9393	35–38	199·3	99·8	0·7	—	39–41	35–36	209·5	101·1
Tame Rabbit	0·9343	40–42	202·6	67·6	2·8	95·5	40–42	37–39	218·1	64·4

The fat of the rabbit is a yellowish-grey butter-like substance, which, on standing, deposits a "stearine." The fat of the wild animal is characterised by a high iodine value, and has also pronounced drying properties. Thus, Amthor and Zink[1] found that the fat of the wild animal dried to solid varnish when exposed to the air in a thin film on a glass plate for eight to twelve days.

Shea Butter

Shea butter, or karité butter, is expressed from the seeds of *Butyrospermum* (or *Bassia*) *Parkii*, which yield upwards of 40 per cent. of fat.

It is used as an edible fat in West Africa, and is now exported for manufacture into a lard substitute, whilst the "stearine" separated from the fat is used as a chocolate fat.

It is characterised by a high proportion of unsaponifiable matter, 5 to 9 per cent., but methods for removing part of this have now been adopted.

A typical sample examined by Revis and Bolton[2] gave the following results—

Melting point, 41·2 °C.; saponification value, 186·9; refractive index (Zeiss) at 40 °C., 56·3; iodine value, 58·93; free fatty acids (as oleic acid), 8·29 per cent.; and unsaponifiable matter, 7·56 per cent.

[1] *Zeitsch. anal. Chem.*, 1897, xxxvi, 9.

[2] *Allen's Commercial Organic Analysis*, ix, p. 148

CHAPTER VII

BUTTER AND BUTTER FAT

Typical Values

	Specific Gravity.	Saponification Value.	Reichert-Meissl Value.	Hehner Value.	Iodine Value.	Insoluble Fatty Acids.			Soluble Fatty Acids.
						Melting Point °C.	Solidification Point °C.	Molec. Equivalent.	Molecular Equivalent.
English	0·9103–0·9117 at 39° C.	220–228	24–32	87·6	37–39	38–40	33–35	261	98·1
French	0·910–0·9128 at 40° C.	225–229	28–33	—	31–40				
Dutch .	0·9100–0·9128 at 37·8° C.	210–228	17–32	87·6 (lowest)	31–50				

BUTTER

As ordinarily used, the term "butter" refers to the product obtained by churning the milk of the cow, although the fat derived from the milk of the goat, buffalo and other animals is also made into a similar preparation.

Cow's butter contains about 12 to 14 per cent. of water; 84 to 87 per cent. of fat; 0·75 per cent. of casein; 0·5 per cent. of lactic acid; and 0·6 per cent. of salts.

Vieth[1] obtained the following results in the analysis of butters of various origin.

[1] *Analyst*, 1891, xv, 1.

Butter.	Fat per cent.	Curd per cent.	Salt per cent.	Water per cent.
English	86·85	0·59	1·02	11·54
French, fresh . . .	84·77	1·38	0·09	13·76
French, salted . . .	84·34	1·60	2·01	12·05
Kiel	85·24	1·17	1·35	12·24
Danish	83·41	1·30	1·87	13·42
Swedish	83·89	1·33	2·03	13·75

Legal Standards for Butter.—The maximum permissible amount of water in butter has been fixed at 16 per cent. in England, Canada, Queensland, the United States and Germany (salted butter), at 15 per cent. in Victoria, and at 18 per cent. in Belgium and Germany (unsalted butter).

The proportion of fat must not fall below 80 per cent. in Queensland, Victoria and Germany; 82 per cent. in Italy; 82·5 per cent. in the United States.

In Italy butters showing a Reichert-Meissl value of 26 or more are regarded as pure, those with a value of 20 to 26 as suspicious; and those with a value below 20 as adulterated.

In the United States the Reichert-Meissl value must not fall below 24.

Regulations have also been made in different countries for permissible limits of the specific gravity and other constants of the fat.

Colouring Matters

Among the colouring matters which have been used to impart a rich colour to butter are annatto, turmeric, saffron, carrot, safflower and various aniline dyestuffs. The following systematic method of testing for these was devised by Leeds.[1] (*See* table next page.)

A simple method of distinguishing between annatto and coal-tar dyes has been devised by Doolittle:[2]—The fat is melted, and two portions of about 2 c.cm. dissolved in ether in test tubes. One solution is treated with an equal amount of dilute (1:3) hydrochloric acid, and the other with dilute

[1] *Analyst*, 1887, xxii, 150.
[2] *U.S. Dept. Agric.*, *Bur. of Chem.*, *Bull.*, lxv. 152.

(1:10) potassium hydroxide solution, and the tubes are shaken and allowed to stand. In the presence of annatto the alkali tube will show a yellow aqueous layer, whilst in the presence of azo-dyes the acid tube will show a reddish aqueous layer.

Colour.	Sulphuric Acid.	Nitric Acid.	Nitric and Sulphuric Acids.	Hydrochloric Acid.
Annatto . .	Indigo blue to violet	Blue, becoming colourless	Same	No change or brownish
Turmeric . .	Pure violet	Violet	Violet	Violet to original colour on evaporation
Saffron . . .	Violet to cobalt, changing to red-brown	Light blue to light red-brown	Same	Yellow to dirty brown
Carrot . . .	Amber-brown	Decolorised	Same, with NO_2 fumes and odour of burnt sugar	No change
Marigold . .	Dark olive-green	Blue, changing at once to dirty yellow-green.	Green	Green to yellowish-green
Safflower . .	Light brown	Partly decolorised	Decolorised	No change
Aniline yellow	Yellow	Yellow	Yellow	Yellow
Martius yellow	Pale yellow	Yellow, reddish ppt. Magenta at margin	Yellow	Yellow ppt.; treated with ammonia and ignited deflagrates
Victoria yellow	Partly decolorised	Partly decolorised	Same	Same. Colour returns on neutralisation with ammonia

Aniline azo colours soluble in oils are now frequently used for colouring butter and its substitutes.

In some countries, notably the United States, the addition of such colouring matters to margarine is prohibited, and recourse has therefore been had to oils and fats of a pronounced yellow colour, such as oil of mustard and palm oil for colouring these products. Hence these fats may find their way into adulterated butter.

For the detection of small amounts of palm oil, Crampton

and Simons[1] have devised a method, based upon the separation from that oil of a substance giving a blue coloration when tested with acetic anhydride and sulphuric acid.

In the Liebermann-Storch method, which is also based upon a test used for the detection of rosin oils, the filtered fat, which must not have been heated above 70° C., is mixed with an equal quantity of acetic anhydride, and the mixture shaken with one drop of sulphuric acid (sp. gr. 1·53) and allowed to stand. In the presence of palm oil the lower layer which separates will be greenish-blue.

PRESERVATIVES

The preservative most frequently employed in butter is boric acid or a borate. It may be accurately estimated by the following method devised by Richmond and Harrison[2] and Richmond and Miller[3]:—

Twenty-five grms. of the butter are mixed with 10 to 15 c.cm. of chloroform in a stoppered graduated cylinder, and water is added in sufficient quantity to bring the total volume of water up to 25 c.cm. After separation of the two layers (with the aid of centrifugal force, if necessary), 20 c.c. of the aqueous layer (corresponding to 20 grms. of the butter) are withdrawn, and mixed with 10 c.cm. of a 0·5 per cent. solution of phenolphthalein in 50 per cent. alcohol. The mixture is boiled, and titrated, while still boiling, with N/10 sulphuric acid until colourless, and then with N/10 sodium hydroxide solution until slightly pink again, when 25 c.c. of glycerin or 2 grms. of mannitol are added, and the titration completed with the standard alkali. The percentage of boric acid is calculated by means of the formula—

$$(x - y) \times 0{\cdot}0062 \times 5,$$

where x represents the number of c.cm. of alkali used for the final titration, and y the number consumed by the glycerin or mannitol added to the liquid.

For a qualitative test about 1 c.cm. of the aqueous layer

[1] *Analyst*, 1905, xxx, 250. [2] *Ibid.*, 1902, xxvii, 179.
[3] *Ibid.*, 1907, xxxii, 144.

separated from the butter is evaporated with a drop of hydrochloric acid, and a few drops of an alcoholic solution of turmeric. The well-known purple red coloration is obtained in the presence of 0·02 per cent. of boric acid.

Among other preservatives which have been detected in butter are salicylic acid, benzoic acid, fluorides and β-naphthol.

Salicylic Acid may be detected by the violet coloration which is produced when the melted butter is shaken with a solution of ferric chloride.

Benzoic Acid.—The aqueous layer, separated as described above, is acidified with dilute sulphuric acid, and shaken with 20 c.cm. of ether. The ethereal extract is washed with a little water, and treated with 10 c.cm. of water containing a drop of phenolphthalein solution, and neutralised with a saturated barium hydroxide solution. The aqueous layer is withdrawn, and about 2 c.cm. are treated with a few drops of very dilute acetic acid, and then with a few drops of ferric chloride solution. In the presence of benzoic acid (0·1 per cent.), the well-known buff-coloured precipitate is obtained.

Fluorides may be detected by evaporating 10 c.cm. of the aqueous layer and igniting the residue. The ash is moistened with sulphuric acid, and the crucible is covered with a watch-glass, the underside of which is partially coated with paraffin wax, and allowed to stand on a hot plate for two hours. If fluorides are present, the unprotected surface of the glass will be etched.

β-Naphthol.—On mixing the aqueous layer with an emulsion of diazotised naphthionic acid, the immediate appearance of a crimson coloration indicates the presence of β-naphthol.

The reagent is prepared by boiling about 0·2 grm. of 1-4-naphthionic acid with 10 c.cm. of 50 per cent. alcohol, chilling the liquid with ice, and adding 1 c.cm. of dilute sulphuric acid (1:3), and then, little by little, about 10 c.cm. of a 10 per cent. solution of potassium nitrite. After about five minutes the mixture, which should be yellow, is filtered, and the precipitate washed with a little water and mixed with about 5 c.cm. of water. The resulting emulsion will detect less than 0·02 per cent. of β-naphthol.

Pure butter gives a similar coloration gradually in this test, but in the presence of β-naphthol, or abrastol, the reaction takes place immediately.

RENOVATED BUTTER

In the United States, stale butter which has become unsaleable is remelted and churned again with milk, and sold under the name of "renovated" or "process" butter. By this means, a product closely resembling fresh butter in its chemical and physical properties is obtained.

Cochran[1] found that in this treatment the fat assumed a definite crystalline structure, which could be identified under the microscope.

Another test has been based by Hess and Doolittle[2] upon the behaviour of the curd when the product is heated over a flame. In the case of process butter, the material splutters, but does not froth like genuine fresh butter. There is also a pronounced difference in the characteristics of the two curds: that from genuine butter being an amorphous gelatinous mass, whereas the curd from "process" butter is granular and flaky, and is readily soluble in acids and alkalis.

A further distinction depends upon the ratio of the casein to the albumins.

BUTTER FAT

COMPOSITION

Butter fat is composed of the glycerides of a large number of fatty acids and is particularly characterised by its high percentage of volatile soluble acids.

The fatty acids from a sample of Danish butter were found by Koefoed[3] to consist approximately of: Butyric acid, 1·5; caproic acid, 2·0; caprylic acid, 0·5; capric acid, 2·0; lauric acid, 8·0; myristic acid, 22; palmitic acid, 28; stearic acid, 2·0; and oleic acid with acids of the formulæ $C_{15}H_{28}O_4$ and $C_{29}H_{54}O_5$, 34 per cent. Total fatty acids 91·5 per cent.

[1] *Journ. Franklin Inst.*, 1899, cxlvii, 85.
[2] *J. Amer. Chem. Soc.*, 1900, xxii, 150.
[3] *Analyst*, 1892, xvii, 130.

Browne[1] calculated from his results that a sample of butter fat had the following composition—

	Fatty Acids.	Glycerides.
Insoluble Fatty Acids.	Per cent.	Per cent.
Dihydroxystearic acid . . .	1·83	1·04
Oleic acid	32·50	33·95
Stearic acid	1·83	1·91
Palmitic acid	38·61	40·51
Myristic acid	9·89	10·44
Lauric acid	2·57	2·73
Soluble Acids.		
Capric acid	0·32	0·34
Caprylic acid	0·49	0·53
Caproic acid	2·09	2·32
Butyric acid	5·45	6·23

There is good evidence for the conclusion that butter fat contains mixed glycerides (*see* p. 5).

The proportion of stearic acid in butter fat appears frequently to be very small, and various observers found quantities ranging from about 0·49 to 3 or 4 per cent. in the insoluble fatty acids.

This was supported by the results of Hehner and Mitchell,[2] who in some cases obtained no deposit at all, and in others only a very slight one.

Using Hehner and Mitchell's method, however, with the modification of adding pure stearic acid to prevent supersaturation (p. 53), Holland, Reed and Buckley[3] found the insoluble fatty acids of various samples of butter fat to contain from 7 to 22 per cent. of stearic acid.

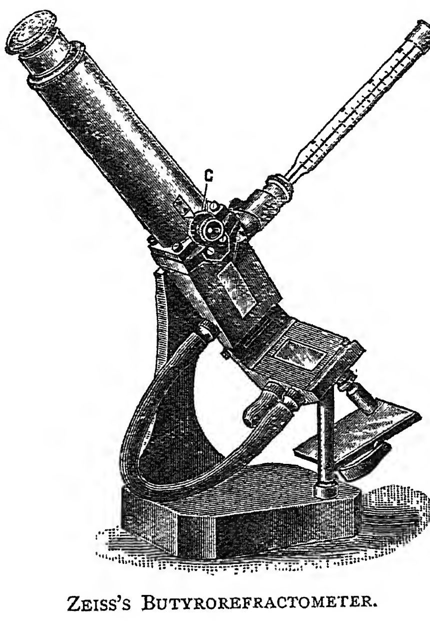
An interesting observation was, that the proportion of stearic acid varied with the nature of the food given to the cows. For example, cows fed with beef tallow yielded butter with insoluble fatty acids containing from 15·2 to 17·56 per cent., whilst the amounts from the butter of cows fed with palm oil were 13·8 to 14·9 per cent., and those from the butter of animals fed with material poor in fat averaged 8·7 per cent.

[1] *J. Amer. Chem. Soc.*, 1899, xxi, 807.
[2] *Analyst*, 1896, xxi, 329. [3] *Ibid.*, 1916, xxi, 209.

THE REFRACTIVE INDEX

One of the most useful tests for rapidly distinguishing genuine from adulterated butter is the determination of the refractive index of the fat. This is conveniently made by means of the Zeiss *butyrorefractometer*, in which the value is determined at a specified temperature, usually 45° C., on an arbitrary scale.

In this instrument the light is reflected from the mirror into one component of the double prism (here shown open),



ZEISS'S BUTYROREFRACTOMETER.

and passing through a film of the fat upon the surface of that prism, enters the other component shown below the screw, C. These prisms are so adjusted that the coloured border-line of total reflection for a particular substance (in this case, pure butter-fat) is rendered achromatic; so, on looking through the telescope, a well-defined vertical border-line is seen.

In the presence of a substance, such as a foreign fat, for which the adjustment of the prisms has not been calculated, the border-line will appear more blue or more red according to whether the refractive power of the substance is higher or lower than the standard substance, and will occupy a different position in the field.

In using this refractometer the prism-casing is opened by turning a screw, so that the lower half of the casing can be lowered, until checked by a support, as shown in the figure. The melted filtered fat is now spread in a uniform layer over the surface of the prism and the casing again closed, so that the space between the two prisms is completely filled.

A tube conveying water at the required temperature is connected with the opening in the side of the prism case, so that the fat is maintained at a constant temperature throughout the observation. The position of the border-line is then read upon the scale, the tenths of a degree being found by turning the micrometer screw C.

Thorpe[1] has devised a convenient form of apparatus for supplying a constant stream of tap water at a regulated temperature to a butyrorefractomer. As is shown in the accompanying diagram, the water passes through the copper or "compo" coil C, which is heated by the steam generated in the vessel, A, and thence flows through the pressure tubing, G, to the refractometer, Z, its rate of flow being controlled by the screw clamp, H. The water is kept at a constant head before entering the coil, by means of the device, E.

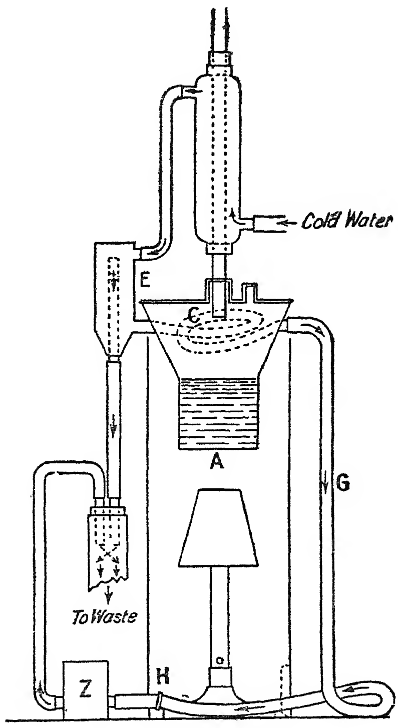
Richmond[2] has described a method of preparing a chart by means of which the readings at one temperature may be converted into those at another.

The refractometer readings obtained by Thorpe in the examination of 371 samples of English butter of various origin ranged from 37·3 to 43·0 at 45° C.; and readings of 42·0 to 47·6 have been recorded for Dutch butters.

[1] *J. Chem. Soc.*, 1904, lxxxv, 257.
[2] *Analyst*, 1907, xxxii, 44.

The Reichert-Meissl Value

This value is one that may afford an immediate proof of the purity of butter fat, though, as a rule, it has to be considered in association with other tests.



Thorpe's Thermostat.

The values obtained by Thorpe[1] with 357 samples of English butter fat ranged from 22·5 to 32·6.

The value for butter from cows which have been left in the fields to a late period of the year before stalling is often low (*e.g.* 20·1), and to this cause is attributed the abnormally low results sometimes obtained in the examination of Dutch butter.

[1] *J. Chem. Soc.*, 1904, lxxxv, 254.

The following results given by Thorpe illustrate the variations which may take place in the value at different periods of the year. The samples were of British origin and from numerous sources.

	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.
Minimum	26·5	26·0	22·5	23·4	22·4	22·3	23·3	23·9	25·6	22·0	27·1	25·3
Maximum	32·8	32·8	31·4	30·5	29·5	29·6	32·9	30·4	31·0	31·6	34·3	33·1

The addition of margarine made from animal fats lowers the Reichert-Meissl value, but this may be corrected, to a considerable extent, by the addition of coconut oil or palm-kernel oil, each of which has a fairly high value (*see* pp. 76, 86). To detect the presence of these fats, the estimation of the amount of volatile fatty acids insoluble in water (Polenske value) is used (*see infra* and Chapter IV, p. 47).

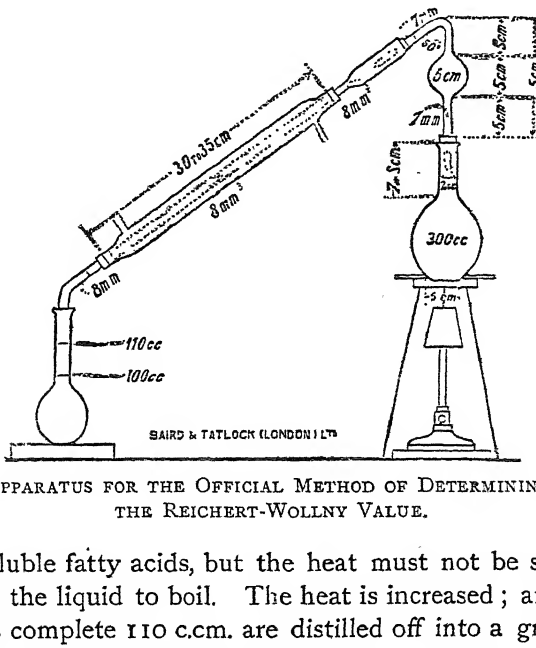
Official Method.—An official method of making the Reichert-Meissl test, as modified by Wollny, (p. 46) has been prescribed by the Government Laboratory and a Committee of the Society of Public Analysts. An apparatus of standard dimensions must be used, and the exact details of working must be closely followed.[1]

The different parts of the apparatus must be of the form and exact dimensions shown in the diagram :—

"Five grms. of the liquid fat are introduced into a 300 c.cm. flask, of the form seen in the figure (length of neck 7 to 8 c.mm., width of neck 2 c.mm.). Two c.cm. of a solution of caustic soda (98 per cent.) in an equal weight of water—preserved from the action of atmospheric carbonic acid—and 10 c.cm. of alcohol (about 92 per cent.) are added, and the mixture is heated under a reflux condenser connected with the flask by a T-piece, for fifteen minutes, in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.cm. of boiling water, which have been kept boiling for at least ten minutes, are added,

[1] *Analyst*, 1900, xxv, 309.

and the flask heated until the soap is dissolved. Forty c.cm. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 mm. wide and 15 c.mm. from the top of the cork to the bend. At a distance of 5 c.mm. above the cork is a bulb 5 c.mm. in diameter. The flask is supported on a circular piece of asbestos, having a hole in the centre 5 c.mm. in diameter, and is first heated by a very small flame, to fuse



Apparatus for the Official Method of Determining the Reichert-Wollny Value.

the insoluble fatty acids, but the heat must not be sufficient to cause the liquid to boil. The heat is increased; and when fusion is complete 110 c.cm. are distilled off into a graduated flask, the distillation lasting about thirty minutes (say from twenty-eight to thirty minutes), the distillate is shaken, 110 c.cm. filtered off, transferred to a beaker, 0·5 c.cm. of phenolphthalein solution (1 grm. in 100 c.cm. of alcohol) added, and the filtrate titrated with decinormal soda or baryta solution. Precisely the same procedure (with the same reagents), omitting the fat, should be followed, and the amount of decinormal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.cm. The volume of decinormal

solution of alkali used, less the figure obtained by blank experiment, is multiplied by 1·1. The number so obtained is the "Reichert-Wollny Number."

"*Notes on the Method.*—The sample is melted and filtered from curd and water through a dry filter. From the filtrate the 5 grms. of fat for the process are taken. The soda solution is filtered clear from carbonate formed in its preparation and kept in a special bottle. The Soxhlet spherical condenser is a convenient one for the reflux distillation. This is fixed near the water-bath in which the saponification is to take place, and is connected with the flask by means of a T-piece and india-rubber tubes inclined at an angle of 45°. During the saponification the free limb of the T-piece is directed upwards, and its end closed by a short piece of india-rubber and glass rod. At the end of fifteen minutes this limb is turned downward, and the piece of glass rod replaced by a tube carrying away the alcohol.

"One hundred c.cm. of hot distilled water are added, and the flask frequently shaken until the soap is dissolved. The Liebig is a convenient form of condenser. One containing a column of water 30 to 35 c.mm. in length gives sufficient condensing surface. After shaking the distillate, about 5 c.cm. are filtered through a dry filter into a 100 c.cm. flask. This serves to wash out the flask. When the 100 c.cm. are transferred to a beaker, the flask is not washed out, but the main quantity is neutralised with the standard solution of alkali, and returned to the flask, then again transferred to the beaker, and the titration completed."

The following are typical Reichert-Meissl values—

Butter fat, 24·1 to 33·2; beef fat, 0·3; coconut oil, 6·6 to 7·5; maize oil, 4·2; palm oil, 0·8 to 1·9; palm-kernel oil, 5 to 6·8; sesamé oil, 1·2; whale oil, 0·7 to 2·0.

The use of fats, such as coconut oil and palm-nut oil for margarine has made it necessary to make an allowance for the volatile fatty acids in these fats, when estimating the proportion of butter fat in margarine.

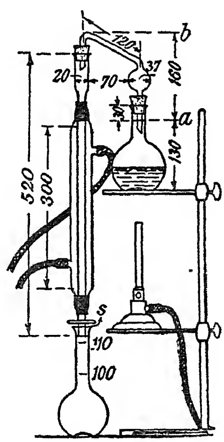
In a Report dated November 7, 1900, it was proposed that a Reichert-Wollny figure, obtained in the specified manner,

should not exceed 4, and that any such excess should be regarded as evidence of butter fat in excess of 10 per cent.

In a further Report[1] the Committee recommended the addition of the following words to their original Report: "The limiting figure of 4, obtained by the Reichert-Wollny method described, and the table of figures connected therewith, are not applicable to those margarines in which the insoluble volatile acids number exceeds 1."

Coconut and Palm-kernel Oil in Butter

The Polenske Value (p. 47) is determined by means of the apparatus shown in the accompanying figure, each part being of the exact dimensions indicated.



POLENSKE'S STANDARD APPARATUS.

It is also essential to the obtaining of concordant and trustworthy results that the process should be carried out in the following manner:—Five grms. of the filtered butter fat are heated over a free flame in a 300 c.cm. flask with 20 c.cm. of glycerine and 2 c.cm. of a solution of one part of sodium hydroxide in one part of water. The soap solution is allowed to cool below 100° C., diluted with 90 c.cm. of water, and heated on the water-bath at about 50° C., until the soap

[1] *Analyst*, 1909, xxxiv, 514.

dissolves. The hot soap solution, which must be clear and practically colourless, is treated with 50 c.cm. of dilute sulphuric acid (25 c.cm. of strong acid per litre) and a few fragments of pumice, and the flask is connected with the condenser as shown in the diagram.

The flask is then heated in such a way that from 19 to 20 minutes are required for the distillation of 110 c.cm., and the temperature of the distillate falling into the flask must not exceed 20° to 23° C.

After 110 c.cm. have been collected, the flask is replaced by a 20 c.cm. graduated cylinder, and, without shaking, is immersed nearly to the top in water at 15° C. After about five minutes, any oily drops on the surface of the liquid are made to adhere to sides of the flask by gently tapping the neck, and the flask is left for a further ten minutes in water. It is then closed with a cork and gently inverted several times, so as to effect thorough admixture of its contents, a note being taken of the character of the insoluble fatty acids (*i.e.* whether semi-solid or oily).

Of this distillate, 100 c.cm. are filtered through a paper 8 c.mm. in diameter, and the filtrate is titrated with N/10 potassium hydroxide solution, as in the ordinary method of determining the Reichert-Meissl value.

The insoluble volatile acids on the filter are washed with three successive portions of 15 c.cm. of water, each of which has been passed through the condenser tube, the 20 c.cm. cylinder and the flask, and the washings, containing the soluble volatile acids, are thrown away. The insoluble volatile acids adhering to the inside of the condenser tube, the sides of the cylinder and the walls of the flask, are removed by three successive rinsings (15 c.cm. each time) with neutralised 90 per cent. alcohol. These washings are poured over the filter, each being left to drain off before the next is added, and the alcoholic filtrate is titrated with N/10 alkali solution.

This method of estimating the volatile insoluble acids by Polenske's process has the drawback that there is some risk of losing the acids deposited within the condenser tube during

the process of washing them out with alcohol. To obviate this Blichfeldt[1] has devised a special form of apparatus, in which the distillation flask is connected with the side tube of an inverted vertical condenser, upon the base of which two bulbs are blown. After the distillation, the bulbs are washed out with standard sodium hydroxide solution, the excess of which is titrated with standard acid.

The insoluble silver salts of the distilled fatty acids are then precipitated by means of a definite quantity of silver nitrate, the precipitation being accelerated by the addition of sodium nitrate. The liquid is made up to a definite volume and filtered, and the excess of silver in an aliquot part of the filtrate is titrated with standard sodium chloride solution. The difference between the equivalent of the total volatile acids and the equivalent of the acids yielding insoluble silver salts, gives the equivalent of the soluble silver salts.

In this way the following results were obtained—

	Total Volatile Fatty Acids.	Soluble Silver Salts.	Insoluble Silver Salts.
Butter	32	29	3
Coconut oil . . .	20	4	16
Palm-kernel oil . .	15	3	12

The method of Shrewsbury and Knapp[2] is based upon the fact that the predominating fatty acid of coconut oil (lauric acid) is readily soluble in dilute alcohol (50 c.cm. of methylated spirit of sp. gr. 0·822 and 36 c.cm. of water at 15° to 17° C.), and may be estimated by titrating the solution with standard alkali solution.

On titrating 70 c.cm. of the alcoholic filtrate with N/10 sodium hydroxide solution, the following results were obtained with pure triglycerides: Tributyrin, 0; trilaurin, 176; trimyristin, 51; tripalmitin, 16; tristearin, 6, and triolein, 65 c.cm. Coconut oil gave a value of 163, whilst 14 samples of pure butter gave results ranging from 23·6 to 31·2, the average being 27·7.

[1] *J. Soc. Chem. Ind.*, 1910, xxix, 792.
[2] *Analyst*, 1910, xxxv, 385.

The fat from cream gave a value of 30, and lard a value of 15·7, so that the method would detect the presence of "nut lard" in lard.

A mixture of butter (average value 25) with 5 per cent. of coconut oil gave a value of 33, whilst with 15 per cent. it gave 38·0 c.cm.

In calculating the proportion of coconut oil from these figures the results were about 5 per cent. too high.

The method is also applicable to the detection of coconut oil in margarine in which the Reichert-Wollny value suggests the presence of more than 10 per cent. of butter.

Turbidity Temperature of Barium Salts.—A method of detecting and approximately estimating coconut and palm-kernel oil in admixture with other fats has been based on the degree of solubility in alcohol of the barium salts of the volatile insoluble acids.[1]

The Polenske value is determined in the usual way by the standard method, with the exception that N/10 baryta solution is used for the titration. The insoluble barium salts are washed with 93 per cent. alcohol (sp. gr. 0·8235 at 15° C.), and dissolved in ten times the quantity in c.cm. of the Polenske value of the boiling alcohol, the flask being heated beneath a reflux condenser.

The temperature at which 5 c.cm. of the solution become turbid when stirred in a closed test-tube is then ascertained.

Under these conditions, coconut oil gave a turbidity temperature of 52·5° C. and palm-kernel oil 58·5° C., whilst mixtures of the two fats gave results corresponding with the percentage composition. Palm-kernel "oleine" and "stearine" gave values of 59·5 and 72·5 respectively. Cohune oil gave the same values as coconut oil.

This method is open to the same objection as the Valenta acetic acid test, viz., that the strength of the solvent must be accurately ascertained at each estimation, since slight variations in the strength of the alcohol will affect the turbidity temperatures.

[1] Burnett and Revis, *Analyst*, 1913, xxxviii, 255.

CHAPTER VIII

HARDENED OR HYDROGENATED OILS

FOR very many years a method of transforming fluid oils into solid fats, on a commercial scale, was eagerly sought in many directions. Although certain processes partially solved the problem and converted part of the fluid oil into solid material, none of them was entirely satisfactory. They yielded, it is true, a substance of higher melting point, which was thus of greater value for the manufacture of candles, but the cost of working the processes was considerable, and the products were only suitable for technical purposes.

On the face of it the problem appears simple enough, for the typical liquid fatty acid, oleic acid, only differs in elementary composition from the typical solid fatty acid, stearic acid, in containing two atoms less of hydrogen. And since oleic acid and its glyceride olein are unsaturated bodies, and will readily absorb and form addition compounds with many chemical elements and compounds such as chlorine or sulphuric acid, there would seem to be no reason why they should not also absorb hydrogen and become stearic acid or stearin.

But for some reason oleic acid can be converted more readily into halogen or sulphur compounds than into the solid hydrogenated compound. Even in the case of the reactions which gave solid derivatives of oleic acid, the yields were far from being quantitative, although in some instances they were considered sufficiently satisfactory to make the processes commercially profitable.

Commercial Processes of the Past.—One of the most interesting commercial ventures on these lines was that undertaken at Radisson's works in France about thirty years ago.

The process was based upon the fact that when oleic acid is fused with potassium hydroxide it is transformed into the solid fatty acid, palmitic acid, while hydrogen is set free (*see* p. 15). The operation was a somewhat dangerous one, owing to the large amount of hydrogen that was liberated, and the results were never in agreement with theoretical expectation. A further drawback was that the product was discoloured in the process, and was thus of inferior value. Evidently these difficulties proved insuperable, for after a short time the process was abandoned.

Sulphuric Acid Processes.—Much better results were obtained in practice by processes in which the oleic acid was saturated with sulphuric acid at a low temperature, and the resulting compound decomposed with water. The combined sulphuric acid was thus set free again, while a white, solid fatty acid, hydroxystearic acid, could be separated from the water and sulphuric acid. And this product, when distilled, yielded a mixture of oleic acid and a solid isomeride, *isoleic acid* (*see* p. 18).

Numerous patents have been taken out for processes upon these lines, and have proved of commercial value for the preparation of solid candle material from fluid oils. As in the case of other processes, however, a considerable quantity of unaltered material was left, and much skill was required to obtain good yields. Although at one time extensively used, it is probable that the sulphuric acid process has now been entirely replaced by methods of hydrogenation.

Hardening of Oils.—The solution of the problem dates back to the investigations of Sabatier and Senderens,[1] who found that when certain unsaturated compounds were treated with hydrogen in the presence of a catalytic agent, such as finely divided platinum or palladium, the combination of the gas with the unsaturated body was readily brought about, while the platinum or other catalyst apparently remained unaffected.

As soon as this fact had been definitely established as applicable to oils it became the basis of commercial processes,

[1] *Comptes rend.*, 1900, cxxx, 723; cxxxi, 187.

and numerous modifications have been patented during the last few years.

The earliest patent in which claim is made for the hydrogenation of oils appears to be that of Le Prince and Liveke, which was taken out in 1902 in Germany. The following year a process upon similar lines was patented by Normann in this country (Eng. Pat. No. 1515, 1903). The vapours from fatty acids were conducted, together with hydrogen, through a bed of porous pumice stone which had previously been incorporated with a catalytic agent, such as fine nickel powder.

In a later process devised by Bedford (Eng. Pat., No. 9112 of 1908), the fatty acids, mainly oleic acid, are sprayed into a tower containing two porous beds of catalytic material, where they meet with hydrogen heated to about 200° C., under reduced pressure. Neither this process, nor that of Normann, is suitable for the hydrogenation of oils, since they involve the vaporisation of the fatty material, which would necessarily involve more or less decomposition of the glycerides.

This drawback is obviated in a German patent taken out by Erdmann in 1907, in which the oil is sprayed in the form of a fine rain into a chamber containing a nickel catalytic agent on pumice or other medium, the temperature being meanwhile maintained at 170° to 180° C.

In another patent of German origin (Eng. Pat., No. 18,642 of 1911), the use of metallic palladium is claimed in place of nickel as a catalyst, and it is stated that the presence of one part of the former metal is sufficient to effect the hydrogenation of 100,000 parts of fluid oil into a solid fat.

The later patents deal mainly with mechanical variations for bringing the hydrogen, oil and catalyst into effective contact. For example, in Kayser's process (U.S. Pat. 1,004,035 of 1911), the oil is agitated with the catalyst in a horizontal cylinder, in which is made to revolve a paddle wheel, the blades of which are covered with wire gauze, while hydrogen is passed through the cylinder, the internal temperature of which is maintained at about 150° to 160° C.

In Wilbuschewitsch's apparatus (1912) the oil is admitted

in the form of a fine spray into connected autoclaves, or pressure tanks, where it meets with a current of hydrogen under a pressure of about nine atmospheres, and is rapidly hydrogenated in the presence of a catalyst at temperatures between 100° and 160° C. The advantage claimed for this process is that, owing to the high pressure employed, hydrogenation is rapidly effected at a relatively low temperature, so that the properties of the oil will not be materially affected.

In the process of Bedford and Williams (U.S. Pat. 1,026,339 of 1912), the oil is mixed with about one per cent. of a metallic catalytic agent, preferably nickel oxide, and is heated in a tank by means of a steam coil to about 250° C., while hydrogen is admitted through openings in a pipe at the bottom of the tank.

Another modification is that devised by Schlink & Co. (Eng. Pat., No. 8147 of 1911), in which the oil and hydrogen are driven by centrifugal force through a series of drums containing a porous material on which is deposited a palladium catalyst.

In Ellis's patent (U.S. Pat., No. 1,026,156 of 1912), tubes are charged with the porous catalytic material, and the oil is pumped through these and meets a current of hydrogen coming from the opposite direction, while the tubes are heated to the desired temperature at any given point.

Details of other forms of apparatus may be obtained from the outline given by Ellis.[1]

A novel process is described by Lessing in Eng. Pat., No. 18,998 of 1912, according to which hydrogen containing 5 to 10 per cent. of carbon monoxide, as would be obtained from water gas, is passed over reduced nickel, whereby nickel carbonyl is formed. The mixture of this with hydrogen is conducted into the oil and heated to about 200° to 240° C., with the result that the nickel carbonyl is decomposed, leaving metallic nickel in a very active condition. Good results are obtained by treating the oil with 0·1 per cent. of nickel.

Catalysts for Hydrogenatian.—The metallic substances in

[1] *J. Soc. Chem. Ind.*, 1912, xxxi, 1155.

most general use for hydrogenating oils are nickel, or its salts, and palladium, although copper, iron, and other metals are claimed for the purpose in several of the patent processes.

Although nickel is perhaps not so effective as palladium for this purpose, its lower cost has caused it to be more generally employed.

When used in the metallic form it is prepared by reducing the nickel oxide, or hydroxide, by means of hydrogen at a temperature exceeding 250° C., the best results being obtained at a temperature a little above 300° C. The activity of the catalytic agent is increased by distributing it over a porous material such as pumice stone, kieselguhr, or charcoal, for it is then brought into more intimate contact with the particles of oil. Its activity is checked or even destroyed by the presence of impurities such as free mineral acids, liquid hydrocarbons, hydrogen phosphide or arsenic in the hydrogen.

Although palladium is a more expensive catalytic agent than nickel, it has been preferred for many purposes, owing to the fact that it will effect the hydrogenation at a much lower temperature (80° to 90° C.) and in a very much shorter time.

Paal[1] found that colloidal palladium preparations effected very rapid hydrogenation of olive and fish oils and animal fats. Platinum black is much less effective than palladium as a catalyst.

The hydrogen for the preparation of the catalyst and for the hydrogenation of the oil is manufactured in large works, either by passing steam over reduced iron, or by the electrolytic decomposition of water.

Characteristics of Hydrogenated Fats.—The properties of hydrogenated oils vary according to the extent to which the hydrogenation has been carried. For example, if the process is stopped after a short time, while a considerable proportion of the liquid glycerides remains unsaturated, a fat of the consistence of butter or lard is obtained, whilst by continuing the hydrogenation, products resembling the hardest tallows are formed.

[1] *Ber.*, 1908, xli, 2282.

The hydrogenation process does not materially affect the acid value, saponification value, or the amount of unsaponifiable matter, but reduces the hydroxyl value of such oils as castor oil.

It also interferes with the distinctive reactions of certain oils, such as the silver nitrate test and Halphen's test for cotton-seed oil, but it does not destroy the sesamol of sesamé oil, which is the active agent in Baudouin's test.[1]

Arachidic acid may be detected by separating the insoluble lead soaps, and recrystallising their fatty acids from alcohol. If their melting point exceeds 70° C., the presence of arachis oil may be inferred.[1]

Hydrogenated fish oils cannot be detected with certainty by the insoluble bromide test, since after the treatment they yield a much smaller proportion of bromides.

In the case of certain marine animal oils, such as whale oil, however, Grimme[2] has found that when the hydrogenated products are dissolved in a mixture of benzene and xylene, and shaken with the usual reagents, they give distinctive colorations, the intensity of which decreases with the degree of hydrogenation. For example, whale oil gives a violet red coloration when tested with sulphuric acid and iodine tincture.

As phytosterol and cholesterol are not affected by hydrogenation, it is still possible to detect the presence of an animal fat by the cholesteryl acetate test.

Grimme[3] gives the following values of a typical hard and soft fat prepared by hydrogenating a marine animal oil :—

Specific Gravity.	Melting Point ° C.	Solidification Point ° C.	Refractive Index at 40° C.	Acid Value.	Saponification Value.	Iodine Value.
0·9271	47·2	34·9	1·4529	1·94	189·3	23·24
0·9200	38·5	31·6	1·4575	1·00	188·8	58·34

However carefully prepared, hydrogenated oils will contain

[1] Kreis and Roth., *Zeitsch. Nahr. Genussm.*, 1913, xxv, 81; *Analyst*, 1913, xxxviii, 160.
[2] *Chem. Rev. Fett Ind.*, 1913, xx, 155.
[3] *Ibid.*, 129; *Analyst*, 1913, xxxviii, 373.

a trace of the metallic catalyst, which is usually nickel. The best method of detecting this is by the dimethylglyoxime test,[1] although it is necessary to take into account that certain untreated oils free from nickel may give a similar coloration in the test (Prall).

The following results were obtained by Sandelin[2] in the examination of hydrogenated fats prepared from whale oil in Germany, and intended for use in the manufacture of margarine:—

	Melting Point ° C.	Solidification Point ° C.	Acid Value.	Saponification Value.	Iodine Value.	Reichert-Meissl Value.	Molecular Weight of Insoluble Fatty Acids.	Melting Point of the Arachidic Acid ° C.
Original whale oil	Fluid	Fluid	9·50	192·2	144·8	0·27	287·7	—
Artificial tallow	47·5	38·1	9·88	183·7	56·9	0·25	296·4	75·5
Artificial stearine	54·3	47·3	7·80	187·7	11·7	0·14	297·0	74·1
Hydrogenated whale oil	41·9	31·9	5·30	190·9	57·8	0·18	282·0	76·0

In each case the hydrogenated oils gave a positive reaction when tested for nickel with dimethylglyoxime.

Use of Hydrogenated Oils for Food.—The now simple process of producing a hard fat from a liquid oil has led to the substitution of such hydrogenated oils for the mixtures of fats and oils which were previously used for such purposes as artificial lard and margarine (*see* p. 118). For products which formerly consisted of cotton-seed oil with sufficient oleostearin to make the mixture semi-solid, cotton-seed oil alone, hardened to the desired extent by hydrogenation, is now frequently employed. Some manufacturers blend hydrogenated oils with fats which have not been hydrogenated, the hardened oil thus taking the place of oleostearin, but in the opinion of Ellis[3] it is preferable to use a single oil hydrogenated to the necessary consistence, since the resulting product is superior both as regards its keeping properties and its palatability.

[1] See Knapp, *Analyst*, 1913, xxxviii, 102.
[2] *J. Soc. Chem. Ind.*, 1914, xxxiii, 1097.
[3] *Ibid.*, 1912, xxxi, 1165.

The presence of traces of nickel in hydrogenated fats is a matter of some importance in connection with their use for food purposes. The nickel combines with the free fatty acids in the oil to form a soluble nickel soap, which remains in the oil when the insoluble nickel catalyst is separated after the hydrogenation.

Ellis (*loc. cit.*) lays stress upon the importance of using the nickel catalyst in the metallic form and not as nickel oxide, since metallic nickel cannot combine with free fatty acids to form a soap, except with the elimination of free hydrogen; and in the presence of an atmosphere of free hydrogen such liberation would be unlikely to occur. He also suggests that the hydrogenation should not be effected too rapidly, so as to prevent decomposition of the fat with the liberation of water, which would react and form fatty acids.

In the case of the hydrogenated fats examined by Bömer[1] considerable proportions of nickel were found. Thus, hydrogenated sesamé oil, with 2·5 per cent. of free fatty acids contained 0·01 per cent. of ash, with 0·006 per cent. of nickel oxide; whilst a specimen of hardened whale oil with 0·6 per cent. of free fatty acids contained 0·006 per cent. of ash and 0·0045 per cent. of nickel oxide.

Offerdahl[2] found that hardened whale oil usually contained from 0·5 to 2 mgrms. of nickel—the maximum amount being 4 mgrms.—per kilo. In his experiments, as much as 0·5 grm. of nickel oxide powder was taken daily without ill-effects, 99·8 per cent. of the metal being rapidly excreted from the system. In his opinion, hardened whale oil is quite suitable for food.

It would be advisable, however, to fix a maximum limit for the permissible amount of nickel in edible fats, as has been done in the case of arsenic in other products.

In other respects, hydrogenated vegetable oils or marine animal oils appear to be as digestible as untreated fats of a similar consistence.

[1] *Chem. Rev. Fett Ind.*, 1912, xix, 221.
[2] *Ber. deutsch. pharm. Ges.*, 1913, xxiii, 558.

At the same time, since the characteristic odour of fish and marine animal oils is liable to reappear in the hydrogenated fats on keeping, it is probable that such hardened fats are less suitable than hydrogenated cotton-seed and sesamé oils for food,

In Germany, prior to 1914, the factories where the two classes of products were made were kept quite distinct. A technical product known as *candelite* was made from whale and fish oils, whilst an edible fat termed *talgol* was prepared from vegetable oils.

Klimont and Mayer[1] discussing the use of hydrogenated fish oils for margarine are of opinion that the principal objection is the possible recurrence of the odour.

As a test for the presence of hydrogenated fish oil they dissolve 2 to 3 grms. of the sample in 50 c.cm. of acetone, and weigh the amount of deposit which is formed after twelve hours. Under these conditions, oleomargarine yields 12 to 13 per cent. of crystals melting at 45° to 47° C., whilst, when mixed with hydrogenated fish oil, the amount exceeds 12 to 16 per cent., which may be accepted as the limit for genuine oleomargarine.

It seems probable that it would be a simple matter to stop the hydrogenation process at an earlier stage, and thus render this test valueless, whilst an addition of arachis oil to the margarine would probably increase the amount of the deposit given by oleomargarine to a greater extent than in the case of hydrogenated fish oil.

[1] *Zeitsch. angew. Chem.*, 1914, xxvii, 645.

CHAPTER IX

MANUFACTURE OF MARGARINE

THE preparation of an artificial substitute for butter, by Mège-Mouries, dates back about fifty years, and his invention was fully utilised during the siege of Paris in 1870. In the original process the fatty material was cut up and mixed with a solution of potassium carbonate, and the minced stomach of a sheep or pig, so as to effect a partial digestion of the cellular substance. This enabled the fat to be "rendered" at a relatively low temperature which would not affect its flavour. The more solid glycerides which deposited as the melted fat cooled, were separated by means of a press from the more fluid portions, and the latter were coloured and flavoured, and used as a butter substitute.

The name *margarine*, which is now the legal term for all kinds of artificial butter, owes its origin to the fact that it was, at the time of its invention, believed to consist largely of "margarin," the glyceride of "margaric acid," which Chevreul concluded was one of the principal constituents of most natural fats. Later research by Heintz, and others, showed that Chevreul's margaric acid was, in the main a mixture of stearic and palmitic acids, but the name of the commercial product still survived, and was chosen for legislative purposes as being more unlike the word "butter" than such terms as "butterine."

In the modern methods of preparing margarine the process of artificial digestion is omitted, the animal fat being rendered at a carefully regulated low temperature in a chamber heated to about 50° C.; or it is finely divided and heated with water at a still lower temperature. The more

fluid fat which first separates from the tissue is drawn off, whilst the residual fatty tissue is afterwards heated to a higher temperature to separate the more solid fat. The fluid portion is chilled in order to cause a partial crystallisation of the more solid glycerides, and is then pressed whereby it is separated into a solid residue known as "beef stearine" and a semi-solid fat which goes by the name of "oleomargarine." As a rule, this is softer than butter, but sometimes contains too much stearine to be suitable for direct conversion into margarine. In such cases it is rendered more fluid by the addition of a suitable proportion of a vegetable oil, such as cotton-seed, arachis, or sesamé oils.

The animal fat most frequently used for the preparation of margarine is beef suet, but lard stearine is also a common ingredient of American margarine (*see* pp. 29, 30).

Until a comparatively recent date, most of the margarine of commerce was made from a basis of animal fat, rendered as described above, and thinned to the desired extent. This was churned with a suitable quantity of fresh or sour milk and colouring matter, until the desired degree of firmness and the butter flavour was obtained, and was then rapidly cooled, and made into small parcels for sale.

At the present time, solid vegetable fats, more particularly those derived from the fruits of various species of palm, are also widely employed as ingredients of margarine, whilst deodorised coconut oil is used in the preparation of both margarine and "nut butter" (*see* p. 33).

According to a Trade Report,[1] the amount of margarine made in Denmark in 1911 was 78,043,630 lbs. Since 1908 a change has taken place in the nature of the ingredients, the raw material then consisting of about 70 per cent. of animal fat and 30 per cent. of vegetable fat, whereas at the present time it consists of about 70 per cent. of vegetable fat and 30 per cent. of animal fat. Coconut oil, expressed from copra in Denmark, is used in large quantities for this purpose.

In some of the inferior qualities of margarine large additions of stale butter were present a few years ago, this butter

[1] *Oil, Paint and Drug Rep.*, Oct. 28, 1912.

being churned up with the fat milk and flavouring reagents so as to produce a substance which could be readily mistaken for a genuine inferior butter.

The addition of butter fat to margarine is now restricted to a maximum of 10 per cent., which is permissible for flavouring purposes (*see* p. 103).

The following were the proportions of the constituents of different grades of margarine made in the United States[1] prior to the introduction of hydrogenated oils—

HIGH GRADE MARGARINE

	Parts.
Oleomargarine	100
Neutral lard	130
Butter	95
Salt	32
Colouring matter	0·5
	357·5

Yielding about 352 parts of margarine.

MEDIUM HIGH GRADE MARGARINE

	Parts.
Oleomargarine	315
Neutral lard	500
Cream	280
Milk	280
Salt	120
Colouring matter	1·5
	1496·5

Yielding from 1350 to 1380 parts of margarine.

CHEAP GRADE MARGARINE

	Parts.
Oleo oil	495
Neutral lard	265
Cotton-seed oil	315
Milk	255
Salt	120
Colouring matter	1·25
	1451·25

Yielding from 1265 to 1300 parts of margarine.

[1] *Census Bulletin.*

The production of solid fats by the hydrogenation of oils has recently added other sources of material to those previously available for the manufacture of margarine. The use of such hydrogenated oils for this purpose in place of oleomargarine has been patented by Deveaux (Fr. Pat., 458,611 of 1913). According to an American trade report[1] most of the larger manufacturers of "compound lard," who formerly used a mixture of 80 per cent. of cotton-seed oil with 20 per cent. of oleostearine, now use cotton-seed oil alone, after hydrogenation to the desired extent.

Hardened cotton-seed oil is also used to a limited extent in Europe for the manufacture of margarine. Attempts have been made to use hydrogenerated fish oils for this purpose, but, as was mentioned before, the odour of the oil which has been removed by the hydrogenation is liable to reappear after some time.

Emulsification of the Fat.—An essential condition for the production of margarine of the best quality is to have the fat particles broken up into a state of the finest emulsion with the milk serum, so as to produce the physical characters of butter fat.

A machine extensively employed for this purpose is known as the *margarine churn.* It consists of a jacketed cylinder, within which are rotating cylinders, and is provided with inlets for steam and water, so that the temperature of the mixture can be regulated to the desired point.

Milk is first introduced into the cylinder while the agitators are rotating, and after it has been brought to the most suitable temperature for the particular fat to be churned, this fat, or mixture of fats, is introduced, and the agitation is continued until an emulsion is formed.

The contents of the cylinders are now chilled by the admission of cold water into the jacket, and, when only a little above the solidification point, the emulsion is transferred from the churn to the cooling apparatus.

The margarine churn is still constructed upon very similar lines to the earlier machines, although modifications in the

[1] *Oil, Paint and Drug Rep.*, July 20, 1914.

driving machinery and the form of the agitators have been introduced. It has the drawback of being relatively large in proportion to the quantity of material emulsified, and of requiring a considerable amount of power for driving.

Hence, numerous attempts have been made to devise an improved emulsifying machine. One of the earliest of these apparatus is Schroeder's *Emulsifier* (Eng. Pat. 25,404 of 1905), which is used in many factories for continuous emulsification of the margarine mixture.

The churning vessel of the machine is much smaller than the usual margarine churn, and contains two agitators, which rotate at a high speed. The milk and the fat mixture are introduced through an inlet at the top, and are beaten by the agitators into a fine emulsion, which is then gradually forced downwards by the agitator blade and discharged through an outlet at the bottom.

After leaving the churn, the emulsion passes through another apparatus where it is further subdivided, and, in some cases, can be made up into packages without further cooling, other than effected in storage.

In some factories this homogenising apparatus is omitted, and several churns of the same type are connected together, through which the margarine mixture passes without interruption, to be discharged from the last one in the form of a thick cream.

Another type of continuous emulsifier is that invented by Silkeborg (Eng. Pat. 4657 of 1914). This is a horizontal cylinder surrounded by a heating jacket, and containing a shaft, on which are several blades. As these rotate at a high speed, they drive the mixture of milk and fat against the surface of perforated baffle plates fixed between the blades. The emulsion is forced through these holes on to the next baffle plates, and so on, until it leaves the cylinders at the opposite end. The holes in the successive baffle plates decrease in size.

Among other recent forms of emulsifiers mention may be
of Blichfeldt (Eng. Pat. 18,048 of 1914). This
ith a rotating disc pierced with slots, which is

mounted on a hollow shaft in a vessel, the walls of which are close to the sides of the disc. The milk, or other fluid containing serum, is introduced through the hollow shaft, while the melted fat is delivered through openings in a tube which passes across the vessel.

Cooling the Emulsion.—After the fat has been thoroughly emulsified with the milk serum and other ingredients, it is rapidly cooled, and for this purpose separate apparatus is generally employed.

The process of cooling in use may be described as the wet or the dry method. In the former, ice-water, or, rather, water chilled to a low temperature by refrigerating tanks, is used as the cooling medium. In a common type of apparatus, the emulsion leaving the churn is delivered in a thin film on to a sloping trough, where it meets a stream of water at about 4° C., and falls as a solidified mass into a tank, where it is skimmed off the surface of the water by means of wooden blades.

Various modifications of the cooling devices are in use, such as rollers, travelling bands, etc. In an apparatus devised by Rasmussen (Eng. Pat. 29,831 of 1913) a thin film of the melted fatty mixture is distributed on to the surface of a hollow cylinder, which rotates in cold water to a depth of about two-thirds of its diameter. As the fat congeals on the upper part of the cylinder, it is removed by means of scrapers, which deposit it on a travelling band.

In some factories, cooled skim-milk or buttermilk is used instead of water, to prevent some of the aromatic products, formed in the milk during the fermentation, from being washed out of the margarine. A further drawback to the water-cooling method is that it may remove some of the proteins from the milk, and thus reduce the food value of the product.

This process is also unsuitable for chilling mixtures containing such fats as palm-kernel oil and coconut oil, since unless very rapidly cooled these fats yield a product of crystalline structure.

For fatty mixtures of this type, the method of cooling the emulsion by means of chilled air gives more satisfactory results.

For example, the melted emulsion may be distributed on to the surface of a travelling band, which traverses a casing, through which passes a current of cold filtered air (Eng. Pat. 20,292 of 1911). In some cases, the temperature of the emulsion is brought as low as $-7°$ C. (Eng. Pat. 17,613 of 1913).

In the apparatus devised by Christensen and Lauridsen (Eng. Pat. 20,568 of 1912) the emulsion is distributed on to the surface of a rotating cylinder, the thickness of the deposit being regulated by a movable iron bar. A current of chilled brine circulates through the interior of the cylinder, and the cooled deposit is mechanically removed by a fixed scraper.

In a similar type of apparatus patented by Jurgens (Eng. Pat. 10,863 of 1914) a revolving cylinder, through which circulates warm water of the same temperature as the emulsion, dips into the mixture, and carries on its surface a certain quantity, which it transfers to the cooling cylinder. This has a diameter of 8 to 10 times that of the feeding cylinder, and the thickness of the coating of emulsion may be regulated by varying the speed at which the feeding cylinder revolves. Both cylinders revolve in the same direction, and the process is continuous.

After being cooled by one or other of these processes, the margarine, which frequently has a more or less crystalline structure, requires mechanical kneading to convert it into a soft butter-like mass.

In some margarine factories care is taken to prevent contact of the material with impure air throughout the entire process (*e.g.* Blichfeldt, Eng. Pat. 4508 of 1912).

Aroma and "Browning" Properties.—In order to give an aroma similar to that of butter, cultivations of various species of bacteria are sometimes added to the milk with which the fat is to be churned (Poppe, Eng. Pat. 18,500 of 1898). Or a small proportion of volatile fatty acids from pure butter fat may be introduced.

Wilson (Eng. Pat. 24,051 of 1911) employs a flavouring agent obtained by the action of bacteria on a mixture of

casein and lactose in such proportion that no excess of either remains after the bacterial action.

A similar bacterial process has been patented by Schou (Eng. Pat. 4504 of 1913).

With the object of making margarine resemble butter in its frothing and "browning" properties when heated, the addition of various substances has been claimed, such as, for example, egg-yolk alone or emulsified with sugar, almond milk or other vegetable product containing emulsin, or vegetable wax.

Addition of Colouring Matters.—Margarine is coloured with vegetable or aniline yellow dyestuffs, or with palm oil (*see* pp. 85, 92).

In some countries, the addition of a "latent" colour is enforced. That is to say, the product must contain a substance, such as phenolphthalein, which will enable it to be readily recognised on the addition of a reagent.

For the same reason, the addition of 10 per cent. of sesamé oil is obligatory in Germany, so that the margarine will give a characteristic reaction in the Baudouin test (*see* p. 69).

Objection has been taken to this plan on the grounds that certain vegetable dyes may give a similar pink coloration, and that it is possible for cows fed upon sesamé cake to yield butter which gives a slight reaction in the test.

The general methods of detecting margarine in butter are given in the sections dealing with butter fat and the individual oils and fats.

BIBLIOGRAPHY

General Handbooks

C. R. Alder Wright and C. A. Mitchell. *Animal and Vegetable Fixed Oils, Fats, Butters and Waxes. Their Preparation and Properties.* 2nd Ed. London, 1903. Griffin.

A. H. Allen. *Commercial Organic Analysis.* 4th Ed. Vols. II and IX, 1910 and 1916. London. Churchill.

J. B. Leathes. *The Fats.* (Monographs on Biochemistry.) London, 1910. Longmans.

J. Lewkowitsch. *Chemical Technology and Analysis of Oils, Fats and Waxes.* 5th Ed., 3 vols. London, 1915. Macmillan.

——. *Thorpe's Dictionary of Applied Chemistry.* Longmans.

C. Revis and E. R. Bolton. *Fatty Foods.* London, 1913. Churchhill.

L. Ubbelohde. *Handbuch der Chemie und Technologie der Oele und Fette.* 4 Vols. Leipzig, 1908 *et seq.* Hirzel.

F. Ulzer and J. Klimont. *Chemie der Fette.* Berlin, 1906.

CHAPTER I

THE NATURE, PROPERTIES AND COMPOSITION OF FATS

Mono-, Di- and Tri-glycerides

Geitel. J. prakt. Chem., 1897, 429; 1898, 113.

J. Lewkowitsch. Ber., 1900, XXXII, 89.

Reimer and Will. Ber., 1886, XIX, 3320.

Action of Heat

H. Masters and H. L. Smith. *The Changes in the Character of Fats during Cooking.* Analyst, 1914, XXXIX, 347.

Mixed Glycerides

Blyth. *Glycerides in Butter Fat.* Proc. Chem. Soc., 1889, 5.

A. Bömer. *Mixed Glycerides of Palmitic and Stearic Acid in Lard.* Zeitsch. Nahr. Genussm., 1913, XXV, 321. (J. Soc. Chem. Ind., 1913, XXXII, 434.)

——. *The Theoretical Basis of Polenske's "Difference Values" of Fats.* Zeitsch. Nahr. Genussm., 1913, XXV, 367. (J. Soc. Chem. Ind., 1913, XXXII, 434.)

A. Bömer and R. Limprich. *The Synthetic Preparation of α-Distearin and β-Palmito-distearin.* Zeitsch. Nahr. Genussm., 1913, XXV, 354. (J. Soc. Chem. Ind., 1913, 434.)
Heise. *Oleodistearin in Mkanyi Fat and Kokum Butter.* Arb. Kaiserl. Gesundheitsamte, 1896, XII, 540; XIII, 302.
R. Henriques and M. Kühne. *The Characteristics of Oleodistearin.* Ber., 1899, XXXII, 387. (Analyst, 1899, XXIV, 185.)
D. Holde. *On the alleged Natural Occurrence of Heptadecylic Acid.* Berlin, 1905, XXXVIII, 1247. (Analyst, 1905, XXX, 215.)
—— and M. Stange. *Mixed Glycerides in Olive Oil.* (Analyst, 1903, XXVIII, 40.)
—— ——. *Mixed Glycerides in Natural Fats.* Ber., 1901, XXXIV, 2402. (Analyst, 1901, XXVI, 324.)
J. Klimont. *The Occurrence of Mixed Glycerides in Cacao Butter.* Ber., 1901, XXXIV, 2636. (Analyst, 1902, XXVII, 15.)
—— and E. Meisels. *The Occurrence of Mixed Glycerides in Natural Fats [Goose and Duck Fats].* Monats. Chem., 1909, XXX, 341. (Analyst, 1909, XXXIV, 363.)
H. Kreis and A. Hafner. *Mixed Glycerides in Lard and Beef and Mutton Fat.* Ber., 1903, XXXVI, 2766. (Analyst, 1903, XXVIII, 359.)
—— ——. *The Composition of Lard and Beef Fat Crystals.* Zeitsch. Nahr. Genussm., 1904, VII, 641. (Analyst, 1904, XXIX, 259.)

Rancidity of Fats

Ballantyne. J. Soc. Chem. Ind., 1891, X, 29.
F. Canzoneri and G. Bianchini. *The Rancidity of Olive Oil and Oxidation of Oleic Acid in Presence of Sunlight.* Annali Chim. Applic., 1914, I, 24. (Analyst, 1914, XXXIX, 255.)
J. Hanus and A. Stocky. *On the Chemical Action of the Growth of Moulds on Butter.* Zeitsch. Nahr. Genussm., 1900, III, 606. (Analyst, 1901, XXVI, 15.)
G. Issoglio. *The Analysis of Rancid Fats.* Annali Chim. Applic., 1916, VI, 1. (Analyst, 1916, XLI, 304.)
H. Kreis. *Bishop's Reaction for Sesamé Oil.* Chem. Zeit., 1899, XXIII, 802. (Analyst, 1900, XXV, 49.)
A. Mjoen. *On the Cause of the Rancidity of Fats.* Forsch, Ber., 1897, IV, 195. (Analyst, 1898, XXIII, 42.)
J. Nagel. *Separation of the Constituents of Rancid Fats and Oils.* Amer. Chem. J., 1900, XXIII, 173. (Analyst, 1900, XXV, 212.)
A. Scala. *Measurement of the Rancidity of Fats other than Butter.* Staz. Sper. Agr. Ital., 1896, XXVIII, 733. (Analyst, 1896, XXI, 298.)
E. Spaeth. *On the Rancidity of Fats.* Zeitsch. anal. Chem., 1896, XXXV, 471. (Analyst, 1897, XXII, 46.)
P. Soltsien. *The Chemical Detection of Rancidity in Butter.* Chem. Rev. Fett Ind., 1905, XII, 177. (Analyst, 1905, XXX, 333.)
H. S. Walker. *On the Rancidity of Coconut Oil.* Philippine J. Science, 1906, I, 117. (Analyst, 1906, XXXI, 165.)

F. Wiedmann. *The Detection of Rancid Fat in Edible Fats.* Zeitsch. Nahr. Genussm., 1904, VIII, 136. (Analyst, 1904, XXIX, 306.)

CHAPTER II

CONSTITUENTS OF OILS AND FATS

A.—FATTY ACIDS

Volatile Fatty Acids

H. Agulhon. *The Detection of Volatile Fatty Acids.* Bull. Soc. Chim., 1913, XIII, 404. (Analyst, 1913, XXXVIII, 274.)

F. W. J. Boekhout and J. J. O. de Vries. *Duclaux's Method for the Estimation of Fatty Acids.* J. Chem. Soc., 1917, CXII, ii, 50.

D. C. Dyer. *Method of Steam Distillation for the Determination of Volatile Fatty Acids, including a Series of Colorimetric Qualitative Reactions for their Identification.* J. Biol. Chem., 1917, XXVIII, 445. (J. Soc. Chem. Ind., 1917, XXXVI, 236.)

Duclaux. Ann. Chim. Phys., 1874, II, 289.

A. R. Lamb. *Note on the Duclaux Method for Volatile Fatty Acids.* J. Amer. Chem. Soc., 1917, XXXIX, 746. (Analyst, 1917, XLII, 214.)

K. Langheld and A. Zeileis. *Analysis of Mixtures of Lower Fatty Acids.* Ber., 1913, XLVI, 273. (Analyst, 1913, XXXVIII, 273.)

H. D. Richmond. *Duclaux's Method for the Estimation of Volatile Fatty Acids.* Analyst, 1895, XX, 198, 217.

——. *Studies in Steam Distillation.* Analyst, 1906, XXXI, 324; 1908, XXXIII, 305; 1917, XLII, 125, 133.

F. W. Upson, H. M. Plum and J. E. Schott. *Duclaux Method for the Estimation of Volatile Fatty Acids.* J. Amer. Chem. Soc., 1917, XXXIX, 731. (Analyst, 1917, XLII, 214.)

Non-Volatile Fatty Acids

Baruch. *Constitution of Oleic Acid.* Ber., 1894, XXVII, 173.

——. *Stearolic Acid.* Ber., 1894, XXVIII, 172.

H. Bull. *Separation of Cod-liver Oil Fatty Acids (Gadolinic Acid).* Ber., 1906, XXXIX, 3570. (Analyst, 1907, XXXII, 25.)

Cloez. (*Elæomargaric Acid.*) Comptes rend., 1875, LXXXI, 469.

A. Hébert. *Isamic Acid: A New Unsaturated Fatty Acid.* Bull. Soc. Chim., 1896, XV, 941. (Analyst, 1896, XXI, 298.)

O. Hehner and C. A. Mitchell. (*Linolenic Acid.*) Analyst, 1898, XXIII, 317.

Ljubarsky. (*Physetoleic Acid.*) J. prakt. Chem., 1898, LVII, 26.

Nordlinger. (*Daturic Acid.*) Ber., 1892, XXV, 578.

F. B. Power and F. H. Gornall. *The Constituents of Chaulmoogra Seeds.* Proc. Chem. Soc., 1903, XX, 264.

M. Tsujimoto. *A New Unsaturated Fatty Acid in Japanese Sardine Oil (Clupanodonic Acid).* J. Coll. Eng., Tokio, 1906, IV, 1. (Analyst, 1906, XXXI, 335.)

SAYTZEFF. (*Constitution of Oleic Acid.*) Ber., 1894, XXVII, Ref. 577.
——. (*Iso-oleic Acid.*) J. prakt. Chem., 1898, LVII, 27.

B.—ALCOHOLS

GLYCERIN

H. BULL. *Estimation of Glycerin in Oils as Sodium Glyceroxide.* Chem. Zeit., 1916, XL, 690. (Analyst, 1916, XLI, 343.)
J. LEWKOWITSCH. *Note on the Estimation of Glycerin.* Analyst, 1901, XXVI, 35.
A. SHUKOFF AND P. J. SCHESTAKOFF. *A Direct Method of Estimating Glycerin.* Zeitsch. angew. Chem., 1905, XVIII, 294. (Analyst, 1905, XXX, 130.)
R. WILLSTÄTTER AND A. MADINAVEITIA. *The Estimation of Glycerin in Fats.* Ber., 1912, XLV, 2825. (Analyst, 1912, XXXVII, 571.)

CHAPTER III

EXTRACTION AND PURIFICATION OF OILS AND FATS

H. WILEY. *Lard and Lard Adulterants.* Rep. U.S.A. Dept. Agric., Bull., XIII, 1889.
VOIGTLÄNDER. *American Lard.* Zeitsch. angew. Chem., 1898, 857. (J. Soc. Chem. Ind., 1898, XVII, 1055.)

CHAPTER IV

METHODS OF EXAMINATION

H. J. BACKER. *Relationship between the Physical and Chemical Constants of Fats.* Chem. Weekblad, 1916, XXXV, 954. (Analyst, 1916, XLI, 315.)
A. SEIDENBERG, *Method for Fractionating Oils and Fats.* J. Ind. Eng. Chem., 1917, IX, 855. (J. Soc. Chem. Ind., 1917, XXXVI, 1138.)

I.—PHYSICAL METHODS

THE SPECIFIC GRAVITY

E. BELLMER. *Determination of the Specific Gravity of Oils.* Chem. Zeit., 1911, XXXV, 997. (Analyst, 1911, XXXVI, 557.)
A. O. RANSOME. *The Effect of Free Fatty Acid on the Specific Gravity of some Fatty Oils.* J. Soc. Chem. Ind., 1912, XXXI, 672.
C. H. WRIGHT. *A Temperature Correction applicable to the Specific Gravities of all Oils, Fats and Waxes.* J. Soc. Chem. Ind., 1907, XXVI, 513.
——. *The Determination of the Specific Gravity of Fixed Oils and Fats in the Tropics.* J. Soc. Chem. Ind., 1916, XXXV, 457.

MELTING AND SOLIDIFICATION POINTS

E. CARLINFANTI AND M. LEVI-MALVANO. *Melting and Solidification Points of Mixtures of Stearic, Palmitic and Oleic Acids.* Gazz. Chim. Ital., 1909, XXXIX, 353. (Analyst, 1910, XXXIII, 30.)

A. Grün. (*Double Melting Point.*) Ber., 1912, XLV, 3691. (J. Soc. Chem. Ind., 1913, XXXII, 95.)
—— and P. Shacht. (*Double Melting Point.*) Ber., 1907, XL, 1778. (J. Soc. Chem. Ind., 1907, XXVI, 536.)
R. Meldrum. *Solidifying and Melting Points of Mixtures of Stearic and Oleic Acids.* Chem. News, 1913, CVIII, 199.
——. *Solidifying Point of Mutton Tallow.* Chem. News, 1915, CXI, 98.
A. Shukoff. *Uniform Method of Tallow Titration.* Chem. Rev. Fett Ind., 1899, VI, 11. (J. Soc. Chem. Ind., 1899, XVIII, 403.)
E. Twitchell. *Melting and Solidifying Points of Mixtures of Fatty Acids and Use of these Points to determine the Composition of such Mixtures.* J. Ind. Eng. Chem., 1914, VI, 564. (Analyst, 1914, XXXIX, 448.)
F. Wolfbauer. *Method for the Determination of the Solidification Point of Fatty Acids.* J. Amer. Chem. Soc., 1894, XVI, 665.

Thermal Tests

The Maumené Test

Ballantyne. J. Soc. Chem. Ind., 1891, IX, 29.
Ellis. J. Soc. Chem. Ind., 1886, V, 361.
W. Marden and M. V. Dover. *The Thermal Values of the Fats and Oils—II. The Maumené Value.* J. Ind. Eng. Chem., 1917, IX, 858. (J. Soc. Chem. Ind., 1917, XXXVI, 1138.)
C. A. Mitchell. *On the Maumené Test for Oils.* Analyst, 1901, XXVI, 176.
Maumené. Comptes rend., XXXV. (J. Soc. Chem. Ind., 1886, V, 150, 361.)
H. D. Richmond. *Maumené's Test for Oils.* Analyst, 1895, XX, 58.
M. Tortelli. *Estimation of the Thermal Value of Fats and Oils.* Chem. Zeit., 1909, XXXIII, 125, 134, 171, 184. (Analyst, 1909, XXXIV, 168.)

Bromine Thermal Method

A. H. Gill and J. Hatch. *Heat of Bromination Test for Oils.* J. Amer. Chem. Soc., 1899, XXI, 27. (Analyst, 1899, XXIV, 97.)
O. Hehner and C. A. Mitchell. *A New Thermal Method for the Examination of Oils.* Analyst, 1895, XX, 146.
J. W. Marden. *Heat of Bromination of Oils and Fats.* J. Ind. Eng. Chem., 1916, VIII, 121. (Analyst, XLI, 176.)
H. Wiley. *Determination of the Heat of Bromination in Oils.* J. Amer. Chem. Soc., 1896, XVIII, 378. (Analyst, 1896, XXI, 210.)
J. A. Wilson. *The Bromine Heat Value of Fats and Oils.* Chem. News, 1896, 87.

Calorimetry of Fats

E. de Schweinitz. *The Use of the Calorimeter in Butter and Lard Analysis.* J. Amer. Chem. Soc., 1896, XVIII, 174. (Analyst, 1896, XXI, 107.)
H. C. Sherman and J. F. Snell. *On the Use of Combustion as a*

Factor in the Analytical Examination of Oils. J. Amer. Chem. Soc., 1901, XXIII, 164. (Analyst, 1901, XXVI, 241.)

ELECTRICAL CONDUCTIVITY OF FATS

L. HERLANT. *The Electrical Conductivity of Oils and Fats.* Bull. de l'Ass. belge Chim., 1896, X, 48. (Analyst, 1896, XXI, 275.)

SOLUBILITY TESTS

Critical Temperature of Solution

A. VON ASBOTH. *On the Critical Temperature of Fats and Oils.* Chem. Zeit., 1896, XX, 685. (Analyst, 1897, XXII, 21.)

L. CRISMER. *A New Method of Analysing Fats and Hydrocarbons.* Bull. de l'Ass. belge Chim., 1895, IX, 71. (Analyst, 1895, XX, 209.)

——. *Critical Temperatures of Solution: A New Constant for the Examination of Fats.* Bull. de l'Ass. belge Chim., 1895, IX, 5, 143. (Analyst, 1895, XX, 257.)

——. *The Critical Temperature of Solution applied to the Analysis of Butter.* Bull. de l'Ass. belge Chim., 1896, X, 312. (Analyst, 1897, XXII, 71.)

—— AND J. MOTTEU. *Saturation Temperatures and Critical Temperatures: Application to General Analysis.* Bull. de l'Ass. belge Chim., 1896, IX, 359. (Analyst, 1896, XXI, 241.)

The Valenta Test

W. CHATTAWAY, T. H. PEARMAIN AND C. G. MOOR. *Note on the Valenta Acetic Acid Test.* Analyst, 1894, XIX, 147.

L. HOTON. *On the Solubility of Glycerides in Acetic Acid.* Bull. Soc. Chim. belge, 1904, XVIII, 147. (Analyst, 1904, XXIX, 284.)

HURST. J. Soc. Chem. Ind., 1887, VI, 22.

E. W. T. JONES. *Turbidity Temperatures of Oils and Fats with Glacial Acetic Acid.* Analyst, 1894, XIX, 151.

THOMPSON AND BALLANTYNE. J. Soc. Chem. Ind., 1891, X, 233.

VALENTA. Dingler's polyt. J., CCLII. (J. Chem. Soc., XLVI, 1078.)

OPTICAL EXAMINATION

REFRACTIVE INDEX

A. G. BREEN. *The Refraction of Butter Fat and its Non-Volatile Fatty Acids.* Zeitsch. Nahr. Genussm., 1908, XV, 79. (Analyst, 1908, XXXIII, 123.)

T. H. PEARMAIN. *The Testing of Oils with the Oleo-refractometer.* Analyst, 1895, XX, 134.

H. D. RICHMOND. *The Temperature Correction of the Zeiss Butyro-refractometer.* Analyst, 1907, XXXII, 44.

L. M. TOLMAN AND L. S. MUNSEN. *Refractive Indices of Salad Oils. Correction for Temperature.* J. Amer. Chem. Soc., 1902, XXIV, 754. (Analyst, 1907, XXVII, 298.)

C. C. ROBERTS. *Zeiss Butyro-refractometer. The Conversion of Scale Readings to Refractive Indices.* Analyst, 1916, XLI, 376.

M. WEGER. *Examination of Oils with the Refractometer.* Zeitsch. angew. Chem., 1899, 297. (Analyst, 1899, XXIV, 158.)

ABSORPTION SPECTRA

PATTERSON. *The Absorption Spectra of Oils.* J. Soc. Chem. Ind., 1890, IX, 36.

ACTION ON POLARISED LIGHT

M. A. RAKUSIN. *The Behaviour of the more important Vegetable Oils towards Polarised Light.* Chem. Zeit., 1906, XXX, 143. (Analyst, 1906, XXXI, 117.)

MOLECULAR WEIGHT DETERMINATION

H. J. BACKER. *Molecular Weights of Certain Vegetable Oils.* Chem. Weekblad, 1915, XII, 1034. (Analyst, 1916, XLI, 47.)

W. NORMANN. *Determination of the Molecular Weight of Oils and Fats.* Chem. Zeit., 1907, XXXI, 214. (Analyst, 1907, XXXII, 124.)

II.—CHEMICAL METHODS

ACID VALUE

E. BÖDTKER. *Estimation of Free Fatty Acids in Fats.* Chem. Zeit., 1911, XXXV, 548. (Analyst, 1911, XXXVI, 355.)

SAPONIFICATION VALUE

A. GRÜN AND O. CORELLI. *Saponification of Fats by Sulphuric Acid.* Zeitsch. angew. Chem., 1912, XXV, 665. (Analyst, 1912, XXXVII, 256.)

R. HENRIQUES. *Saponification in the Cold.* Zeitsch. angew. Chem., 1895, 721; 1896, 221. (Analyst, 1896, XXI, 67, 192.)

——. *Fractional Saponification of Oils and Fats.* Zeitsch. angew. Chem., 1898, 338, 697. (Analyst, 1898, XVIII, 181, 290.)

J. LEWKOWITSCH. *Theory of Saponification.* Proc. Chem. Soc., 1899, 190.

——. *Theory of Saponification.* Ber., 1900, XXXIII, 89. (Analyst, 1900, XXV, 209.)

KOETTSTORFER. Zeitsch. anal. Chem., 1879, XVIII, 199.

A. J. J. VANDEVELDE. *The Fractional Saponification of Fats.* Ann. Falsific., 1912, V, 417. (Analyst, 1912, XXXVII, 559.)

REICHERT VALUE

C. GRIMALDI. *The Influence of Antiseptic Agents on the Reichert-Meissl Value of Fats.* Ann. Lab. Chim. Gabelle, 1912, VI, 631. (Analyst, 1913, XXXVIII, 68.)

A. KIRSCHNER. *Determination of Butter Fat and Coconut Oil in Margarine.* Zeitsch. Nahr. Genussm., 1905, IX, 65. (Analyst, 1905, XXX, 205.)

H. Kreis. *The Determination of the Reichert-Meissl Value of Fats by means of Glycerin Potassium Hydroxide.* Chem. Zeit., 1911, XXXV, 1053. (Analyst, 1911, XXXVI, 542.)

H. Leffmann and W. Beam. *A Modification of the Reichert Distillation Process.* Analyst, 1891, XX, 153.

Meissl. Dingler's polyt. J., CCXXXIII, 229.

Reichert. Zeitsch. anal. Chem., 1879, XVIII, 68.

A. Reychler. *Note on the Reichert Value of Butter and other Fats.* Bull. Soc. Chim., 1901, XXV, 142. (Analyst, 1901, XXVI, 71.)

C. Revis and E. R. Bolton. *Observations on some Methods of Estimating Coconut Oil and Butter in Butter and Margarine.* Analyst, 1911, XXXVI, 336.

M. Siegfried and P. Vieth. *The Reichert-Meissl Value of Butter.* Zeitsch. Nahr. Genussm., 1901.

Wollny. Analyst, 1887, XII, 203.

Polenske Value

Polenske. *A New Method for Determining Coconut Oil in Butter,* Zeitsch. Nahr. Genussm., 1904, VII, 273. (Analyst, 1904, XXIX. 154.)

C. Revis and E. R. Bolton. *Observations on Some Methods of Estimating Coconut Oil and Butter in Butter and Margarine.* Analyst, 1911, XXXVI, 333.

R. R. Tattock and R. T. Thomson. *Value of the Polenske Test in the Analysis of Oils and Fats.* J. Soc. Chem. Ind., 1909, XXVIII, 690.

See also Chapter IX, Butter and Butter Fat.

Iodine Absorption

W. Arnold. *Sources of Error in the Determination of the Polenske Value of Fats.* Zeitsch. Nahr. Genussm., 1912, XXIII, 389. (Analyst, 1912, XXXVII, 256.)

H. Dubovitz. *Preparation of Wijs' Iodine Solution.* Chem. Zeit., 1914, XXXVIII, 1111. (J. Soc. Chem. Ind., 1915, XXXIV, 305.)

J. Ephraim. *On the Hübl Method of Iodine Absorption.* Zeitsch. angew. Chem., 1895, 254. (Analyst, 1895, XX, 176.)

J. Hanůs. *The Use of Iodine Bromide in the Analysis of Oils and Fats.* Zeitsch. Nahr. Genussm., 1901, IV, 913. (Analyst, 1902, XXVII, 15.)

Hübl. Dingler's polyt. J., CCLIII, 281. (J. Soc. Chem. Ind., 1884, III, 641.)

H. Ingle. *Reactions taking place in the Determination of the Iodine Value.* J. Soc. Chem. Ind., 1902, XXI, 587.

W. Mergen and A. Winogradoff. *The Action of Halogens on Oleic Acid and Estimation of the Iodine Value of Fats.* Zeitsch. angew. Chem., 1914, XXVII, 241. (Analyst, 1914, XXXIX, 311.)

G. Ponzio and C. Gastaldi. *Relationship between the Iodine Value and the Structure of Acids of the Oleic Series.* Gazz. Chim. Ital., 1912, XLII, 92. (Analyst, 1912, XXXVII, 463.)

L. M. Tolman and L. S. Munson. *Iodine Absorption of Oils and Fats.* J. Amer. Chem. Soc., 1903, XXV, 244. (Analyst, 1903, XXVIII, 153.)

S. Ueno. *Preparation of Wijs' Iodine Solution.* (J. Soc. Chem. Ind., 1916, XXXV, 367.)

H. T. Vulte and L. Logan. *A Comparison between the Bromine and Iodine Absorption Figures of Various Oils.* J. Amer. Chem. Soc., 1901, XXIII, 156. (Analyst, 1901, XXVI, 240.)

Waller. *The Theory of Hübl's Iodine Process and a Suggestion for its Improvement.* Chem. Zeit., 1895, XIX, 1786, 1831. (Analyst, 1895, XX, 280.)

J. J. Wijs. *The Reactions in Hübl's Method of Iodine Absorption.* Zeitsch. angew. Chem., 1898, 291. (Analyst, 1898, XXIII, 238.)

——. *A New Method for Determining the Iodine Absorption of Oils.* Ber., 1898, XXXI, 750. (Analyst, 1898, XXIV, 2407.)

——. *A Comparison of the Methods of Iodine Absorption in the Analysis of Fats.* Chem. Rev. Fett Ind., 1899, VI, 5. (Analyst, 1899, XXIV, 94.)

——. *On the Determination of the Iodine Value.* Analyst, 1900, XXV, 31.

——. *The Use of Iodine Bromide in the Determination of the Iodine Value.* Zeitsch. Nahr. Genussm., 1902, V, 497. (Analyst, 1902, XXVII, 255.)

St. Weiser and H. C. Donath. *Comparison of Various Methods of Determining the Iodine Value of Fats.* Zeitsch. Nahr. Genussm., 1914, XXVIII, 65. (Analyst, 1914, XXXIX, 406.)

Bromine Absorption

O. Hehner. *On the Determination of the Bromine Absorption of Fats Gravimetrically.* Analyst, 1895, XX, 49.

P. C. McIlhiney. *A New Method of Analysing Fats and Resins.* J. Amer. Chem. Soc., 1894, XVI, 275. (Analyst, 1894, XIX, 141.)

——. *The Determination of the Bromine Absorption of Oils.* J. Amer. Chem. Soc., 1899, XXI, 1084. (Analyst, 1900, XXV, 106.)

E. J. Mills and T. Akitt. *Estimation of Oils and Fats.* J. Soc. Chem. Ind., 1884, III, 65.

—— and J. Snodgrass. *Estimation of Oils and Fats.* J. Soc. Chem. Ind., 1883, II, 436.

R. Williams. *Iodine and Bromine Values of Oils and Fats.* J. Soc. Chem. Ind., 1900, XIX, 300.

Insoluble Bromide Test

A. Eibner and H. Muggenthaler. *The Hexabromide Value of Fatty Oils and the Estimation of Rape Oil in Raw Linseed Oil.*

Farbenzeitung, 1912, XVIII, 131, 175, 235, 356, 411, 466, 523, 582, 641. (Analyst, 1913, XXXVIII, 158.)
A. GEMMELL. *The Insoluble Bromide Value of Oils and its Determination.* Analyst, 1914, XXXIX, 297.
O. HEHNER AND C. A. MITCHELL. *Contributions to the Chemistry of Drying Oils, with a Method for the Examination of Linseed Oil.* Analyst, 1898, XXIII, 315.
J. WALKER AND G. WARBURTON. *Hexabromides of Glycerides and Fatty Acids.* Analyst, 1902, XXVII, 235.
H. R. PROCTER. *Examination of Marine Oils.* J. Soc. Chem. Ind., 1906, XXV, 798.
H. SPRINKMEYER AND A. DIEDRICHS. *The Bromine Absorption of certain Vegetable Oils and Fats.* Zeitsch. Nahr. Genussm., 1912, XXIII, 679. (Analyst, 1912, XXXVII, 403.)
C. STIEPEL. *The Detection of Marine Animal Oil in other Oils and Fats.* Seifenseider Zeit., 1912, XXXIX, 953. (Analyst, 1913, XXXVIII, 35.)
J. A. L. SUTCLIFFE. *Notes on the Insoluble Bromide Test for Drying Oils.* Analyst, 1914, XXXIX, 28.
——. *Note on the Insoluble Bromide Value of Oils.* Analyst, 1914, XXXIX, 388.

ACETYL VALUE

E. B. HOLLAND. *Estimation of the Acetyl Value of Oils, Fats, etc.* J. Ind. Eng. Chem., 1914, VI, 482. (Analyst, 1914, XXXIX, 362.)
J. LEWKOWITSCH. Proc. Chem. Soc., 1890, VI, 72, 91.
——. *The Analysis of Fats; The Acetyl Value.* J. Soc. Chem. Ind., 1897, XVI, 503.
——. *The Meaning of the Acetyl Value in Fat Analysis.* Analyst, 1899, XXIV, 319.
W. NORMANN. *The Determination of the Acetyl Value.* Chem. Rev. Fett Ind., 1912, XIX, 205. (Analyst, 1912, XXXVII, 508.)

ESTIMATION AND SEPARATION OF INSOLUBLE FATTY ACIDS

A. VON ASBOTH. *A Method for Distinguishing between Different Fats.* Chem. Zeit., 1897, XXI, 312. (Analyst, 1897, XXII, 213.)
H. BULL. *The Estimation of Unsaturated Fatty Acids in Marine Animal Oils.* Chem. Zeit., 1899, XXIII, 1043. (Analyst, 1900, XXV, 126.)
DAVID. *The Separation of Solid from Liquid Fatty Acids.* Comptes rend., 1910, CLI, 756. (Analyst, 1911, XXXVI, 22.)
S. FACHINI AND G. DORTA. *Note on the Fatty Acids and Detection of Arachidic Acid.* Chem. Zeit., 1914, XXXVIII, 18. (Analyst, 1914, XXXIX, 122.)
W. FAHRION. *The Composition and Analysis of Linseed Oil Fatty Acids.* Zeitsch. angew. Chem.., 1903, XVI, 1193. (Analyst, 1904, XXIX, 50.

W. Fahrion. *On the Separation of Fatty Acids.* Zeitsch. angew. Chem., 1904, XVII, 1482. (Analyst, 1905, XXX, 97.)

K. Farnsteiner. *The Separation of Saturated from Unsaturated Fatty Acids.* Zeitsch. Nahr. Genussm., 1898, I, 390. (Analyst, 1898, XXIII, 285.)

——. *The Use of Benzene in Determining the Iodine Value of Fats and the Liquid Portion of Fatty Acids. Ibid.*, 529. (Analyst, 1898, XXIII, 288.)

——. *The Separation of Unsaturated Fatty Acids from one another. Ibid.*, 1899, II, 1. (Analyst, 1899, XXIV, 132.)

P. Falciola. *The Separation of Oleic Acid from Stearic and Palmitic Acids.* Gazz. Chim. Ital., 1910, XL, 217, 425. (Analyst, 1911, XXXVI, 23, 114.)

J. Gsell. *The Separation of Saturated Fatty Acids from each other.* Chem. Zeit., 1907, XXXI, 100. (Analyst, 1907, XXXII, 95.)

H. Kreis and E. Roth. *Fractional Precipitation of Fatty Acid Mixtures (Detection of Rape Oil).* Chem. Zeit., 1913, XXXVII, 58. (Analyst, 1913, XXXVIII, 114.)

J. Lewkowitsch. *Note on the Separation of Oleic Acid from other Fatty Acids.* Analyst, 1900, XXV, 64.

F. Muter and L. de Koningh. *Improved Method for the Analysis of Fats.* Analyst, 1889, XIV, 61.

——. *Note on the Analysis of Lard, Cotton Oil, Tallow, etc.* Analyst, 1890, XV, 48.

A. Partheil and F. Ferié. *A New Method of Separating Fatty Acids.* Arch. Pharm., 1903, CCXLI, 545. (Analyst, 1904, XXIX, 51.)

Rose. *Separation of Fatty Acids.* Zeitsch. anal. Chem., 1886. (J. Soc. Chem. Ind., 1887, VI, 306.)

E. Twitchell. *The Separation of Solid and Liquid Fatty Acids.* J. Amer. Chem. Soc., 1895, XVII, 289. (Analyst, 1895, XX, 165.)

——. *On the Estimation of Unsaturated Fatty Acids.* J. Soc. Chem. Ind., 1897, XXVI, 1002.

A. de Waele. *The Fachini-Dorta Method of Separating Liquid from Solid Fatty Acids in Oils and Fats.* Analyst, XXXIX, 389.

T. Zerewitinoff. *The Estimation of Hydroxy Fatty Acids by means of Magnesium Methyl Iodide.* Zeitsch. anal. Chem., 1913, LI, 729. (Analyst, 1914, XXXIX, 41.)

Estimation of Stearic Acid

David. Comptes rend., LXXXVI, 1416.

Heintz. Ann. Chem. Pharm., XCII, 295.

N. H. Emerson. *Solubility of Stearic Acid in Ethyl Alcohol at 0° C.* J. Amer. Chem. Soc., 1907, XXIX, 1750. (Analyst, 1908, XXXIII, 61.)

O. Hehner and C. A. Mitchell. *On the Determination of Stearic Acid in Fats.* Analyst, 1896, XXI, 316.

E. B. Holland, J. C. Read and J. P. Buckley. *Estimation of Stearic Acid in Butter Fat.* J. Agric. Research, 1916, VI, 101. (Analyst, 1916, XLI, 209.)

H. Kreis and A. Hafner. *Estimation of Stearic Acid.* Zeitsch. Nahr. Genussm., 1902, VI, 22. (Analyst, 1902, XXVIII, 115.)

Separation of Cholesterol and Phytosterol

A. Bömer. *The Extraction of Cholesterol and Phytosterol.* Zeitsch. Nahr. Genussm., 1898, I, 21. (Analyst, 1898, XXIII, 42.)

——. *The Detection of Vegetable Oils in Animal Fats by means of the Phytosteryl Acetate Test.* Zeitsch. Nahr. Genussm., 1901, IV, 1070. (Analyst, 1902, XXVII, 94.)

M. Fritzsche. *The Detection of Phytosterol in Animal Fats.* Zeitsch. Nahr. Genussm., 1913, XXVI, 644. (Analyst, 1914, XXXIX, 84.)

O. Forster and R. Riechelmann. *The Detection of Cholesterol in Fats.* Zeitsch. offentl. Chem., 1897, III, 10. (Analyst, 1897, XXII, 131.)

D. D. Kedrovitsch. *The crude Cholesterol of Coconut Oil and the crude Cholesterol of Butter Fat, and the Detection of Coconut Oil in Butter.* Zeitsch. Nahr. Genussm., 1912, XXIV, 334. (Analyst, 1912, XXXVII, 497.)

H. Kreis and O. Wolff. *Extraction of Cholesterol and Phytosterol.* Chem. Zeit., 1898, XXII, 805. (Analyst, 1898, XXIII, 294.)

M. Klostermann. *The Detection of Vegetable Fats in Animal Fats.* Zeitsch. Nahr. Genussm., 1913, XXVI, 437. (Analyst, 1914, XXXIX, 32.)

—— and H. Opitz. *The Estimation of Cholesterol in Fats.* Zeitsch. Nahr. Genussm., 1914, XXVII, 713. (Analyst, 1914, XXXIX, 310.)

—— ——. *Estimation of Phytosterol in Vegetable Oils.* Zeitsch. Nahr. Genussm., 1914, XXVIII, 138. (Analyst, 1916, XLI, 317.)

B. Kuhn, F. Bengen and J. Werwerinke. *The Detection of Phytosterol in Animal Fats by Bömer's Digitonin Method.* Zeitsch. Nahr. Genussm., 1915, XXIX, 321. (Analyst, 1915, XL, 506.)

J. Marcusson. *The Separation of Cholesterol and Phytosterol.* Chem. Rev. Fett Ind., 1901, VIII, 104. (Analyst, 1901, XXVI, 302.)

—— and H. Schilling. *Differentiation of Animal and Vegetable Fats.* Chem. Zeit., 1913, XXXVII, 1001. (Analyst, 1913, XXXVIII, 458.)

A. Olig. *Detection of Phytosterol by Precipitation with Digitonin.* Zeitsch. Nahr. Genussm., 1914, XXVIII, 129. (Analyst, 1916, XLI, 317.)

O. Pfeffer. *Precipitation of Cholesterol and Phytosterol by Digitonin.* Zeitsch. Nahr. Genussm., 1916, XXXI, 38. (Analyst, 1916, XLI, 317.)

E. Ritter. *The Quantitative Separation of Cholesterol and Phytosterol from Fats.* Chem. Zeit., 1901, XXV, 872. (Analyst, 1902, XXVII, 16.)

H. Salomon. *Estimation of the Unsaponifiable Constituents by means of the Digitonin Method.* Ber. deutsch. Pharm. Ges., 1914, XXIV, 189. (Analyst, 1914, XXXIX, 310.)

A. Windaus. *Estimation of Cholesterol and Cholesteryl Esters.* Zeitsch. physiol. Chim., 1910, LXV, 110. (Analyst, 1910, XXXV, 256.)

Alcoholysis of Glycerides

G. D. Elsdon. *Alcoholysis and the Composition of Coconut Oil.* Analyst, 1913, XXXVIII, 8.

——. *Composition of Palm-kernel Oil.* *Ibid.*, 1914, XXXIX, 79.

A. Haller. *Alcoholysis of Fats.* Comptes rend., 1906, CLXXIII, 657. (Analyst, 1907, XXXII, 52.)

—— and Youssouffian. *Alcoholysis of Coconut Oil.* Comptes rend., 1906, CLXXIII, 803. (Analyst, 1907, XXXII, 55.)

Mayer. Chem. Zeit., 1907, XXXI, 793.

Tests of Drying Capacity

W. Bishop. *Determination of the Degree of Oxidation of Oils.* J. Pharm. Chim., 1896, 55. (Analyst, 1896, XXI, 105.)

O. Hehner and C. A. Mitchell. *Contributions to the Chemistry of Drying Oils.* Analyst, 1898, XXIII, 310.

Livache. Comptes rend., 1886, CII, 1167.

L. P. Wilson and G. S. Heaven. *A New Oxygen Absorption Method for Oils.* J. Soc. Chem. Ind., 1912, XXXI, 565.

The Elaidin Test

L. Archbutt. J. Soc. Chem. Ind., 1886, V, 303.

F. G. Edmed. *Action of Dilute Nitric Acid on Oleic and Elaidic Acids.* Proc. Chem. Soc., 1899, XV, 190.

K. Farnsteiner. (*Separation of Individual Fatty Acids in Fats.*) J. Soc. Chem. Ind., 1899, XVIII, 500.

A. P. Lidow. *The Influence of Temperature on the Elaidin Reaction.* (Analyst, 1895, XX, 178.)

CHAPTER V

CHARACTERISTICS OF INDIVIDUAL EDIBLE OILS

Almond Oil

R. Ross and J. Race. *Note on Almond and Apricot-kernel Oils.* Analyst, 1911, XXXVI, 263.

Arachis Oil

J. Bellier. *The Detection and Estimation of Arachis Oil and other Oils.* Ann. Chim. Anal., 1899, IV, 4. (Analyst, 1899, XXIV, 98.)

R. Biazzo and S. Vigdorcik. *The Detection of Arachis Oil in Rape Oil.* Annali Chim. Applic., 1916, VI, 179. (Analyst, 1917, XLII, 85.)

N. Evers. *The Detection and Estimation of Arachis Oil.* Analyst, 1912, XXXVII, 487, 537.

R. H. Kerr. *The Detection of Arachidic Acid.* J. Ind. Eng. Chem., 1916, VIII, 904. (Analyst, 1916, XLI, 381.)

H. Kreis and Roth. *Hardened Oils, and the Detection of Arachidic Acid.* Zeitsch. Nahr. Genussm., 1913, XXV, 81. (Analyst, 1913, XXXVIII, 160.)

L. Lüers. *The Detection of Arachis Oil in Olive Oil by the Franz-Adler Method.* Zeitsch. Nahr. Genussm., 1912, XXIV, 683. (Analyst, 1913, XXXVIII, 58.)

H. Mayer and R. Beer. *The Composition of Arachis Oil.* Monatsh. Chem., 1913, XXXIV, 1195. (Analyst, 1913, XXXVIII, 514.)

Renard. Comptes rend., LXXIII, 1330.

S. P. Sadtler. *Earthnut Oil.* Amer. J. Pharm., 1897, LXIX, 490. (Analyst, 1897, XXII, 284.)

P. Sisley and Frehse. *Diazo Reaction of Vegetable Oils (Arachis Oil in Olive Oil).* Bull. Soc. Chim., 1914, XV, 295. (Analyst, 1914, XXXIX, 228.)

W. B. Smith. *The Application to Solid Fats of Renard's Test for Peanut Oil.* J. Amer. Chem. Soc., 1907, XXIX, 1736. (Analyst, 1908, XXXIII, 50.)

M. Tortelli and R. Ruggeri. *The Detection of Cotton, Sesamé and Arachis Oil in Olive Oil.* Chem. Zeit., 1898, XXII, 600. (Analyst, 1898, XXIII, 273.)

Candle-nut Oil

G. de Negri. *Candlenut Oil.* Oest. Chem. Zeit., 1898, I, 202. (Analyst, 1898, XXIII, 241.)

J. Walker and G. Warburton. *Insoluble Bromides.* Analyst, 1902, XXVII, 237.

Cotton-seed Oil

Bechi. Zeitsch. anal. Chem., 1894, XXXIII, 560.

A. Bömer. *The Detection of Cottonseed Oil in Lard by means of Phytosterol.* Zeitsch. Nahr. Genussm., 1898, I, 544. (Analyst, 1898, XXIII, 283.)

K. Fischer and H. Peyan. *Note on Halphen's Reaction for Cottonseed Oil.* Zeitsch. Nahr. Genussm., 1905, IX, 81. (Analyst, 1905, XXX, 131.)

E. Fulmer. *Notes on Halphen's Test for Cottonseed Oil.* J. Amer. Chem. Soc., 1902, XXIV, 1148. (Analyst, 1903, XXVIII, 79.)

L. Garnier. *A Modification of Halphen's Reaction.* J. Pharm. Chim., 1909, XXIX, 273.

E. Gastaldi. *A Modification of Halphen's Test for Cottonseed Oil.* Ann. Lab. Chim. Gabelle, 1912, VI, 601. (Analyst, 1913, XXXVIII, 68.)

E. Gastaldi. *Notes on Halphen's Reaction for Cottonseed Oil.* Annali Chim. Applic., 1914, II, 203. (Analyst, 1915, XL, 15.)

G. Halphen. *A Characteristic Reaction of Cottonseed Oil.* J. Pharm. Chim., 1897, VI, 390. (Analyst, 1897, XXII, 326.)

D. Holde and R. Pelgry. *The Halphen Reaction for Cottonseed Oil.* Chem. Rev. Fett Ind., 1899, VI, 67, 94. (Analyst, 1899, XXIV, 214.)

R. Marcille. *The Detection of Cottonseed Oil in Olive Oil.* Annal. Falsific., 1910, III, 255. (Analyst, 1910, XXXV, 357.)

H. Matthes and W. Heintz. *The Unsaponifiable Substances in Cottonseed Oil.* Arch. Pharm., 1909, CCXLVII, 161. (Analyst, 1909, XXXIV, 362.)

E. Milliau. (J. Soc. Chem. Ind., 1893, XII, 716.)

N. Petkow. *The Detection of Cottonseed Oil.* Zeitsch. öffentl. Chem., 1907, XIII, 21. (Analyst, 1907, XXXII, 123.)

P. N. Raikow. *The Bechi and Halphen Colour Reactions for Cottonseed Oil.* Chem. Zeit., 1899, XXIII, 1025. (Analyst, 1900, XXV, 105.)

L. Rosenthaler. *Notes on Halphen's Reaction for Cottonseed Oil.* Zeitsch. Nahr. Genussm., 1910, XX, 453. (Analyst, 1910, XXXV, 536.)

Rupp. *Halphen's Reaction for Cottonseed Oil.* (Analyst, 1907, XXXII, 95.)

Utz. *A Modification of Halphen's Test for Cottonseed Oil.* Chem. Rev. Fett Ind., 1913, XX, 291. (Analyst, 1914, XXXIX, 92.)

Linseed Oil

G. D. Elsdon and H. Hawley. *The Detection of Adulteration in Linseed Oil.* Analyst, 1913, XXXVIII, 3, 104.

F. Evers. *Methods for distinguishing between Raw and Boiled Oil.* Chem. Zeit., 1899, XXIII, 334. (Analyst, 1899, XXIV, 158.)

A. H. Gill and A. C. Lamb. *The Analytical Constants of American Linseed Oil.* J. Amer. Chem. Soc., 1899, XXI, 29. (Analyst, 1899, XXIV, 97.)

O. Hehner and C. A. Mitchell. *Contributions to the Chemistry of Drying Oils, with a Method for the Examination of Linseed Oil.* Analyst, 1898, XXIII, 310.

H. Ingle. *Notes on Linseed and other Oils.* J. Soc. Chem. Ind., 1911, XXIII, 344.

H. R. Jensen. *Analytical Examination of Linseed Oil.* Pharm. J., 1911, LXXXVI, 839.

J. F. Liverseege and G. D. Elsdon. *Tests for Linseed Oil and its Adulterants.* J. Soc. Chem. Ind., 1912, XXXI, 207.

P. C. McIlhiney. *A Report upon Linseed Oil and its Adulterants.* Report submitted to the Commissioner of Agricult., New York State, 1901.

H. Mannhardt. *The Oxygen Absorption Test for Linseed Oil.* J. Ind. Eng. Chem., 1913, V, 129. (Analyst, 1913, XXXVIII, 159.)

R. WILLIAMS. *The Proportion of Oxygen present in Linseed Oil both before and after Drying.* Analyst, 1898, XXIII, 253.

MAIZE OIL

A. H. GILL AND C. G. TUFTS. *Sitosterol: A possible Test for Maize Oil.* J. Amer. Chem. Soc., 1903, XXV, 254. (Analyst, 1903, XXVIII, 153.)

H. T. VULTE AND H. W. GIBSON. *Corn Oil.* J. Amer. Chem. Soc., 1900, XXII, 453. (Analyst, 1900, XXV, 272.)

R. WILLIAMS. *Maize Oil.* Analyst, 1900, XXV, 146.

OLIVE OIL

L. ARCHBUTT. *Some Tunisian Olive Oils.* J. Soc. Chem Ind., 1907, XXVI, 453.

——. *Some Algerian Olive Oils.* J. Soc. Chem. Ind., 1907, XXVI, 1185.

——. *Characteristics of neutralised Olive-residuum Oils.* J. Soc. Chem. Ind., 1911, XXX, 5.

W. C. BLASDALE. *On some Californian Oils.* J. Amer. Chem. Soc., 1895, XVII, 935. (Analyst, 1896, XXI, 73.)

R. BIAZZO AND S. VIGDORCIK. *The Detection of Rape Oil in Olive Oil.* Annali Chim. Applic., 1916, VI, 185. (Analyst, 1917, XLII, 86.)

G. HALPHEN. *Detection of Oil extracted by Carbon Bisulphide in expressed Olive Oil.* J. Pharm. Chim., 1905, XXI, 54. (Analyst, 1905, XXX, 313)

F. CANZONERI AND G. BIANCHINI. *Characteristics of Olive Oils extracted with Carbon Bisulphide.* Annali Chim. Applic., 1914, II, 1. (Analyst, 1915, XL, 14.)

D. HOLDE. *On the alleged Natural Occurrence of Heptadecylic Acid.* Ber., 1905, XXXVIII, 1247. (Analyst, 1905, XXX, 212.)

O. KLEIN. *The Characteristics of Olive-kernel Oil.* Zeitsch. angew. Chem., 1898, 847. (Analyst, 1898, XXIII, 284.)

M. MALACARNE. *Colour Reactions of Oils with certain Phenols in presence of Nitric Acid.* Giorn. Farm. Chim., 1913, LXII, 153. (Analyst, 1913, XXXVIII, 433.)

R. MARCILLE. *The Iodine Value of Tunisian Olive Oil.* Ann. Chim. Anal., 1907, XII, 188. (Analyst, 1907, XXXII, 257.)

E. MILLIAU. *The Detection of Carbon Bisulphide in Oils.* Ann. Chim. Anal., 1912, XVII, 1. (Analyst, 1912, XXXV, 101.)

A. SASSERATH. *Moroccan Olive Oil.* Zeitsch. Nahr. Genussm., 1910, XX, 749. (Analyst, 1911, XXXVI, 107.)

M. TORTELLI AND R. RUGGERI. *The Detection of Cotton, Sesamé and Arachis Oils in Olive Oil.* Chem. Zeit., 1898, XXII, 600. (Analyst, 1898, XXII, 273.)

—— AND K. FORTINI. *The Detection of Rape Oil in Olive and other Edible Oils.* Chem. Zeit., 1910, XXXIV, 689. (Analyst, 1910, XXXV, 401.)

K. WEDEMEYER. *Java Olive Oil.* Zeitsch. Nahr. Genussm., 1906, XII, 210. (Analyst, 1906, XXXI, 361.)

Sesamé Oil

J. Bellier. *Two New Colour Reactions for Sesamé Oil.* Chem. Zeit., 1899, XXIII, 802. (Analyst, 1900, XXV, 50.)
Bishop. J. Pharm. Chim., 1889, XX, 244. (J. Soc. Chem. Ind., 1890, IX, 112.)
F. Breinl. *Some New Colour Reactions for Sesamé Oil.* Chem. Zeit., 1899, XXIII, 647. (Analyst, 1900, XXV, 50.)
C. Fleig. *Colour Reactions of Sesamé Oil with Aromatic Aldehydes.* Ann. Chim. Anal., 1909, XIV, 132. (Analyst, 1909, XXXIV, 285.)
W. Kerp. *On the Baudouin Reaction.* Zeitsch. Nahr. Genussm., 1899, II, 473. (Analyst, 1899, XXIV, 246.)
H. Kreis. *Bishop's Reaction for Sesamé Oil.* Chem. Zeit., 1899, XXIII, 802. (Analyst, 1900, XXV, 49.)
——. *Some Colour Reactions of Fatty Oils.* Chem. Zeit., 1902, XXVI, 897, 1014. (Analyst, 1902, XXVII, 330, 363.)
——. *Some Colour Reactions of Sesamé Oil. Sesamol a Constituent of Sesamé Oil.* Chem. Zeit., 1903, XXVII, 108. (Analyst, 1903, XXVIII, 364.)
J. Schnell. *Detection of Sesamé Oil in Arachis Oil.* Zeitsch. Nahr. Genussm., 1902, V, 961. (Analyst, 1902, XXVII, 363.)
A. J. Swaving. *The Detection of Sesamé Oil in Butter from Cows fed on Sesamé Oil.* Zeitsch. Nahr. Genussm., 1903, VI, 107. (Analyst, 1903, XXVIII, 110.)
Villavecchia and G. Fabris. *Furfural as a Reagent for Sesamé Oil in other Oils.* Zeitsch. angew. Chem., 1893, 505. (Analyst, 1894, XIX, 47.)

Sunflower Oil

L. Andés. *The Drying Properties of Sunflower Oil.* Chem. Rev. Fett Ind., XVI, 275. (Analyst, 1910, XXXV, 32.)

Walnut Oil

J. Bellier. *The Detection of Foreign Oils in Walnut Oil.* Ann. Chim. Anal., 1905, X, 52. (Analyst, 1905, XXX, 132.)
L. F. Kebler. *Oil of Walnut.* Amer. J. Pharm., 1901, LXXIII, 173. (Analyst, 1901, XXVI, 163.)

CHAPTER VI

CHARACTERISTICS OF INDIVIDUAL EDIBLE FATS

Bassia Tallow

Bassia Kernels and Fats. Bull. Imp. Inst., 1911, IX, 228. (Analyst, 1912, XXXVII, 54.)
P. Berg and J. Angerhausen. *Unsaponifiable Constituents of Mowrah Fat and the Detection of this Fat in Animal and Vegetable Fats.* Zeitsch. Nahr. Genussm., 1914, XXVII, 723. (Analyst, 1914, XXXIX, 310.)

C. J. BROOKS. *A Note on Enkabang and Teglam Fats and Katio Oil from Sarawak.* Analyst, 1909, XXXIX, 205.

F. JEAN. *The Characteristics of Karité Butter.* Ann. Chim. Anal., 1906, XI, 201. (Analyst, 1906, XXXI, 262.)

C. REVIS AND E. R. BOLTON. Allen's Commercial Organic Analysis, IX, p. 147.

H. SPRINKMEYER AND A. DIEDRICHS. *Analytical Values of some Vegetable Fats.* Zeitsch. Nahr. Genussm., 1912, XXIII, 581. (Analyst, 1912, XXXVII, 349.)

BEEF FAT

A. BÖMER. *Occurrence of Tristearin in Beef and Mutton Tallow.* Zeitsch. Nahr. Genussm , 1907, XIV, 90. (Analyst, 1907, XXXII, 357.)

H. KREIS AND A. HAFNER. *The Composition of Lard and Beef Fat Crystals.* Zeitsch. Nahr. Genussm., 1904, VII, 641. (Analyst, 1904, XXIX, 259.)

MAYER. Wagner's Jahresber., 1880, 844.

K. FARNSTEINER. *The Separation of Unsaturated Fatty Acids from one another.* Zeitsch. Nahr. Genussm., 1899, II, 25. (Analyst, 1899, XXIV, 132.)

O. HEHNER AND C. A. MITCHELL. Analyst, 1896, XXI, 319.

See also LARD.

BORNEO TALLOW

Illipé Nuts and the Sources of Borneo Tallow. Bull. Imp. Inst., 1915, XIII, 335. (Analyst, 1916, XLI, 7.)

H. BECKER. *Illipé Nut Fat.* Zeitsch. öffentl. Chem., 1897, III, 545. (Analyst, 1897, XXII, 327.)

J. KLIMONT. *The Composition of Borneo Tallow.* Monatsh. Chem., 1904, XXV, 929. (Analyst, 1905, XXX, 24.)

CACAO BUTTER

F. FILSINGER. *The Iodine Value of Cacao Butter.* Zeitsch. anal. Chem., 1896, XXXV, 517. (Analyst, 1897, XXII, 96.)

——. *The Chemical Examination of Cacao Butter.* Zeitsch. öffentl. Chem., 1897, III, 34. (Analyst, 1897, XXII, 130.)

S. H. DAVIES AND B. G. MCLELLAN. *The Amount of Cacao Butter in the Cacao Bean.* J. Soc. Chem. Ind., 1904, XXIII, 480.

G. HALPHEN. *The Analysis of Cacao Butter.* J. Pharm. Chim., 1908. XXVIII, 345. (Analyst, 1908, XXXIII, 468.)

D. HOLDE. *The Iodine Value of Cacao Butter.* Zeitsch. anal. Chem., 1897, XXXVI, 163. (Analyst, 1897, XXII, 108.)

J. KLIMONT. *The Occurrence of Mixed Glycerides in Cacao Butter.* Ber., 1901, XXXIV, 2636. (Analyst, 1902, XXVII, 15.)

H. MATTHES AND O. ROHDICH. *The Unsaponifiable Constituents of Cacao Butter.* Ber., 1908, XLI, 19. (Analyst, 1908, XXXIII, 93.)

C. Revis and E. R. Bolton. *A simple Test for differentiating between Cacao Butter and "Green Butter."* Analyst, 1913, XXXVIII, 201.

O. Sachs. *Vegetable Fats used as Substitutes for Cacao Butter in Chocolates.* Chem. Rev. Fett Ind., 1908, XV, 9, 300. (Analyst, 1908, XXXIII, 123.)

A. Strohl. *The Iodine Value and Refractive Index of Cacao Butter.* Zeitsch. anal. Chem., 1896, XXXV, 166. (Analyst, 1896, XXI, 231.)

Chicken Fat

R. Ross and J. Race. *Constants of Chicken and Turkey Fats.* Analyst, 1911, XXXVI, 213.

Coconut Oil

C. Barthel and K. Sondén. *The Detection of Coconut Oil in Butter Fat by means of Polenske's Distillation Method and Bömer's Phytosteryl Acetate Test.* Zeitsch. Nahr. Genussm., 1914, XXVII, 439. (Analyst, 1914, XXXIX, 254.)

E. R. Bolton, H. D. Richmond and C. Revis. *On the Relation between the Kirschner and Polenske Values for Margarines Containing Coconut or Palm-kernel Oils.* Analyst, 1912, XXXVII, 183.

H. R. Burnett and C. Revis. *The Proportionate Determination of Coconut and Palm-kernel Oil in Mixtures.* Analyst, 1913, XXXVIII, 255.

N. C. Cassall and B. H. Gerrans. *Estimation of Coconut Oil in admixture with Butter Fat.* Analyst, 1910, XXXV, 519.

G. D. Elsdon. *The Shrewsbury and Knapp Process for the Estimation of Coconut Oil.* Analyst, 1917, XLII, 72.

E. Ewers. *Detection of Coconut Oil in Butter and Lard, and of Lard in Butter.* Zeitsch. Nahr. Genussm., 1910, XIX, 529 (Analyst, 1910, XXXV, 353.)

G. Fendler. *Detection of Coconut Oil in Butter and Lard.* Zeitsch. Nahr. Genussm., 1910, XIX, 544. (Analyst, 1910, XXXV, 354.)

A. Haller and Youssouffian. *Alcoholysis of Coconut Oil.* Comptes rend., 1906, CLXXIII, 803. (Analyst, 1907, XXXII, 55.)

—— and A. Lassieur. *Occurrence of Odorous Substances in Coconut Oil.* Comptes rend., 1910, CL, 1013. (Analyst, 1910, XXXV, 356.)

J. Hanůs. *A Method of Distinguishing Coconut Oil from Butter and other Fats.* Zeitsch. Nahr. Genussm., 1907, XIII, 18. (Analyst, 1907, XXXII, 89.)

—— and L. Stekl. *The Ethyl Ester Value of Fats: A New Constant for the Detection of Coconut Oil.* Zeitsch. Nahr. Genussm., 1908, XV, 577. (Analyst, 1908, XXXIII, 281.)

E. Hinks. *Detection of Coconut Oil in Butter.* Analyst, 1907, XXXII, 160.

A. Hepner. *The Detection of Coconut Oil in Butter by means of Fendler's Method.* Zeitsch. Nahr. Genussm., 1911, XXI, 754. (Analyst, 1911, XXXVI, 451.)

T. R. Hodgson. *A New Constant for Butter Analysis and the Detection of Coconut Oil in Butter Fat.* Chem. News, 1907, XCVI, 273, 288, 297.

F. Jean. *On the Use of "Silver Value" for the Detection of Coconut Oil in Butter.* Ann. Chim. Anal., 1906, XI, 171. (Analyst, 1906, XXXI, 261.)

O. Jensen. *The Volatile Fatty Acids of Coconut Oil and Butter.* Zeitsch. Nahr. Genussm., 1905, X, 265. (Analyst, 1905, XXX, 397.)

H. Matthes and E. Ackermann. *The Unsaponifiable Constituents of Coconut Oil and its Detection in Butter.* Ber., 1908, XLI, 2100. (Analyst, 1908, XXXIII, 357.)

E. Nockmann. *The Detection of Coconut Oil in Butter by means of Ewers' Method.* Zeitsch. Nahr. Genussm., 1911, XXI, 758. (Analyst, 1911, XXXVI, 451.)

A. Muentz and H. Condon. *Examination of Butters for Adulteration with Coconut Oil.* Ann. Inst. Agron., 1904, III, Part I. (Analyst, 1905, XXX, 155.)

E. Polenske. *The Detection of Coconut Oil in Butter and Lard.* Arbeit. Kaiserl. Gesundheitsamte, 1911, XXXVIII, 402. (Analyst, 1912, XXXVII, 93.)

C. Revis and E. R. Bolton. *Observations on some Methods of Estimating Coconut Oil and Butter in Butter and Margarine.* Analyst, 1911, XXXVI, 333.

L. Robin. *The Detection of Coconut Oil in Cacao Butter.* Ann. Chim. Anal., 1907, XII, 181. (Analyst, 1907, XXXII, 256.)

——. *The Detection of Coconut Oil and Margarine in Butter.* Ann. Chim. Anal., 1906, XI, 454. (Analyst, 1907, XXXII, 47.)

R. Ross. *The Estimation of Coconut Oil in Butter.* Analyst, 1908, XXXIII, 457.

—— and J. Race. *Estimation of Coconut Oil in Butter.* Chem. News, 1908, XCVII, 110.

——, —— and F. Maudsley. *Examination of Shrewsbury and Knapp's Process for the Estimation of Coconut Oil.* Analyst, 1911, XXXVI, 195.

H. S. Shrewsbury and A. W. Knapp. *A Short Method for Detecting and Estimating Coconut Oil in Butter and Margarine.* Analyst, 1910, XXXV, 385.

—— ——. *Notes on Shrewsbury and Knapp's Process for Estimating Coconut Oil.* Analyst, 1912, XXXVII, 3.

Γ. Sundberg. *The Calculation of the Quantity of Coconut Oil present in a Butter from the Polenske Value of the Mixture.* Zeitsch. Nahr. Genussm., 1913, XXVI, 422. (Analyst, 1913, XXXVIII, 558.)

L. Vandam. *The Detection of Coconut Oil in Butter and Margarine.* J. Pharm. Chim., 1901, VI, 273. (Analyst, 1901, XXVI, 320.)

J. WAUTERS. *The Detection of Coconut Oil in Butter.* Bull. de l'Ass. belge, 1901, XV, 25, 131. (Analyst, 1901, XXVI, 128, 292.)

See also BUTTER.

GOOSE FAT.

C. AMTHOR AND J. ZINK. *(Goose Fat.)* Zeitsch. anal. Chem., 1897, XXXVI, 1. (Analyst, 1896, XXII, 75.)

J. ROZSENYI. *Composition of Goose Fat.* Zeitsch. angew. Chem., 1896, 364. (Analyst, 1896, XXI, 235.)

HARE FAT

J. KLIMONT. *The Composition of Hare Fat.* Monatsh. Chem., 1912, XXXIII, 441. (Analyst, 1912, XXXVII, 255.)

HORSE FAT

R. FRÜHLING. *Horseflesh and Horse Fat.* Zeitsch. angew. Chem., 1896, 352. (Analyst, 1896, XXI, 231.)

O. HEHNER AND C. A. MITCHELL. *Determination of Stearic Acid in Fats.* Analyst, 1896, XXI, 328.

J. KLIMONT, E. MEISL AND K. MAYER. *Constituents of Horse Fat.* Monatsh. Chem., 1914, XXXV, 1115. (J. Soc. Chem. Ind., 1915, XXXIV, 668.)

M. RAFFO AND G. FORESTI. *Characteristics of the Fats of Different Animals (Ox, Calf, Sheep, Ass, Horse).* Gazz. Chim. Ital., 1909, XXXIX, 444. (Analyst, 1910, XXXV, 68.)

WITTELS AND WELWART. *Biological Method for Detecting Horse Fats in other Fats.* Seifensied. Zeit., 1910, XXXVII, 1914. (Analyst, 1910, XXXV, 527.)

LARD

W. T. BELFIELD. *The Detection of Beef Fat in Lard.* (Analyst, 1888, XIII, 70.)

A. BÖMER. *The Theoretical Basis of Polenske's "Difference Values" of Fats.* Zeitsch. Nahr. Genussm., 1913, XXV, 367. (J. Soc. Chem. Ind., 1913, XXXII, 434.)

——. *Mixed Glycerides of Palmitic and Stearic Acid in Lard.* Zeitsch. Nahr. Genussm., 1913, XXV, 321. (J. Soc. Chem. Ind., 1913, XXXII, 434.)

—— R. LIMPRICH, R. KRÖNIG AND J. KUHLMANN. *The Detection of Beef Fat in Lard.* Zeitsch. Nahr. Genussm., 1913, XXVI, 559. (Analyst, 1914, XXXIX, 84.)

—— R. KRÖNIG, R. LEY AND H. MERTEN. *The Detection of Beef Fat in Lard.* Zeitsch. Nahr. Genussm., 1914, XXVII, 153. (Analyst, 1914, XXXIX, 171.)

K. FISCHER AND J. WEWERINKE. *The Detection of Beef Fat in Lard by Polenske and Bömer's Methods.* Zeitsch. Nahr. Genussm., 1914, XXVII, 361. (Analyst, 1914, XXXIX, 216.)

E. Fulmer. *On the Reaction of Lard from Cottonseed Meal-fed Hogs with Halphen's Reagent.* J. Amer. Chem. Soc., 1904, XXVI, 837. (Analyst, 1904, XXIX, 315.)

G. Halfpaap. *The Relationship between the Iodine Value and the Refraction of Lard.* Zeitsch. Nahr. Genussm., 1908, XV, 65. (Analyst, 1908, XXXIII, 123.)

O. Hehner and C. A. Mitchell. *Examination of Lard Crystals separated from Ether.* Analyst, 1896, XXI, 328.

H. Kreis and A. Hafner. *Mixed Glycerides in Lard and Beef and Mutton Fat.* Ber., 1903, XXXVI, 2766. (Analyst, 1903, XXVII, 359.)

—— ——. *The Composition of Lard and Beef Fat Crystals.* Zeitsch. Nahr. Genussm., 1904, VII, 641. (Analyst, 1904, XXIX, 259.)

A. Leys. *The Detection of Foreign Fat in Lard.* J. Pharm. Chim., 1907, 289. (Analyst, 1907, XXXII, 179, 335, 384.)

W. Meyer. *Critical Examination of the Iodine Value of Lard.* Zeitsch. öffentl. Chem., 1897, III, 134. (Analyst, 1897, XXII, 189.)

E. Polenske. *The Detection of Certain Animal Fats in Admixture with other Animal Fats.* Arb. Kaiserl. Gesundheitsamte, 1907, XXVI, 445. (Analyst, 1907, XXXII, 382.)

Raumer, von. *The Examination of American Lard.* Zeitsch. angew. Chem., 1897, 210, 247. (Analyst, 1897, XXII, 265.)

H. S. Shrewsbury. *A rapid sorting Test for the Detection of Paraffin Wax in Lard.* Analyst, 1909, XXXIV, 348.

P. Soltsien. *The Halphen Reaction and American Lard.* Zeitsch. öffentl. Chem., 1901, VII, 140. (Analyst, 1901, XXVI, 292.)

H. Sprinkmeyer and A. Diedrichs. *The Detection of Beef and Mutton Fats in Lard by Bömer's Method.* Zeitsch. Nahr. Genussm., 1914, XXVII, 571. (Analyst, 1914, XXXIX, 253.)

W. F. K. Stock. *On the Estimation of Beef Fat in Lard.* Analyst, 1894, XIX, 2.

L. M. Tolman. *The Examination of Lard from Pigs fed on Cottonseed Meal.* J. Amer. Chem. Soc., 1905, XXVII, 589. (Analyst, 1905, XXX, 244.)

H. Wiley. *Lard and Lard Adulterants.* Rep. U.S.A. Dept. Agric. Bull., XIII, 1889.

See also Beef Fat.

Palm Oil

E. R. Bolton and D. G. Hewer. *Some Brazilian Oil Seeds.* Analyst, 1917, XLII, 35.

G. T. Bray and F. L. Elliott. *Some New Oil Seeds derived from American Palms.* Analyst, 1916, XLI, 298.

G. A. Crampton and T. D. Simons. *Palm Oil in Butter.* Analyst, 1905, XXX, 250.

A. H. Gill. *The Crampton and Simons Colour Test for Palm Oil.* J. Ind. Eng. Chem. 1917, IX, 136. (Analyst, 1917, XLII, 216.)

A. Hébert. *The Characteristics of Palm Oil from Different Varieties of Palm.* Bull. Soc. Chim., 1911, IX, 1083. (Analyst, 1912, XXXVII, 55.)

Palm-kernel Oil

A. Heiduschka and A. Burger. *Palm-kernel Oil.* Zeitsch. öffentl. Chem., 1914, XX, 361. (J. Soc. Chem. Ind., 1915, XXXIV, 668.)

See also Coconut Oil, Palm Oil, Butter.

Rabbits' Fat

Amthor and Zuik. *A Contribution to Chemistry of An* Zeitsch. anal. Chem., 1897, XXXVI, 1. (Analyst, 1897, XXII, 75.)

L. Drumel. *The Composition of Rabbits' Fat.* Bull. de l'Ass. belge Chim., 1896, IX, 323.

Shea Butter

Shea Nuts and Shea Butter. Bull. Imp. Inst., 1912, X, 286. (Analyst, 1912, XXXVII, 496.)

C. Revis and E. R. Bolton. Allen's Commercial Organic Analysis, IX, p. 148.

J. E. Southcombe. *Composition of Shea Butter.* J. Soc. Chem. Ind., 1909, XXVIII, 499.

Stillingia Tallow

L. M. Nash. *Note on Chinese Tallow Seed Oil.* Analyst, 1904, XXIX, 110.

CHAPTER VII

BUTTER AND BUTTER FAT

Butter

Composition

J. H. Ball. *The Composition of Irish Butter during the Winter Months.* Analyst, 1907, XXXII, 202.

J. Clarke. *The Composition of Dutch Butter.* Analyst, 1901, XXVI, 113.

H. Faber. *On the Composition of Danish Butter.* Analyst, 1900, XXV, 199.

Grossmann and Meinhard. *The Composition of Dutch Butter.* Zeitsch. Nahr. Genussm., 1904, VIII, 237. (Analyst, 1904, XXIX, 305.)

H. D. Richmond. *The Proximate Composition of Butter.* Analyst, 1894, XIX, 16.

S. H. Trimen. *Egyptian Butter and Samna.* Analyst, 1913, XXXVIII, 242.

P. Vieth. *The Composition of Butter.* Analyst, 1891, XVI, 1.

J. Wauters. *The Composition of Belgian Butter.* Bull. de l'Ass. belge Chim., 1900, XIV, 453. (Analyst, 1901, XXVI, 103.)

A. Zega. *Microscopy of Butter.* Chem. Zeit., 1899, XXIII, 321. (Analyst, 1899, XXIV, 206.)

Colouring Matters

R. W. Cornelison. *Detection of Synthetic Colours in Butter.* J. Amer. Chem. Soc., 1908, XXX, 478. (Analyst, 1908, XXXIII, 421.)

G. A. Crampton and F. D. Simons. *Detection of Palm Oil when used as a Colouring Matter in Fats and Oils.* J. Amer. Chem. Soc., 1905, XXVII, 270. (Analyst, 1905, XXX, 250.)

R. E. Doolittle. *Distinction between Annatto and Coal Tar Dyes.* U.S. Dept. Agric., Bur. of Chem., Bull., LXV, 152.

J. F. Geisler. *Detection of a Yellow Azo Dye used for Artificial Colour of Fats.* J. Amer. Chem. Soc., 1898, XX, 110. (Analyst, 1898, XXIII, 93.)

A. H. Gill. *The Crampton-Simons Colour Test for Palm Oil.* J. Ind. Eng. Chem., 1917, IX, 136. (Analyst, 1917, XLII, 216.)

F. H. Leeds. *Methods of Separation of Colouring Matters in Butter, etc.* Analyst, 1887, XXII, 150.

A. H. Low. *Testing for an Azo Dye in Fats, etc.* J. Amer. Chem. Soc., 1898, XX, 889. (Analyst, 1899, XXIV, 73.)

J. Vandriken. *The Colouring Matter of Butter and Substitutes.* Ann. Pharm., 1901, VII, 110. (Analyst, 1901, XXVI, 232.)

Water in Butter

C. Aschman and J. P. Arend. *The Direct Determination of Water in Butter and other Fats.* Chem. Zeit., 1906, XXX, 953. (Analyst, 1907, XXXII, 21.)

A. C. D. Rivett. *Estimation of Water in Butter.* Chem. News, 1911, CIV, 261. (Analyst, 1912, XXXVII, 51.)

A. J. Vandevelde and A. Stewart. *Water in Butter.* Bull. Soc. Chim. Belg., 1909, XXIII, 95. (Analyst, 1909, XXXIV, 213.)

Preservatives

K. Fischer and O. Greunert. *Influence of Certain Preservatives on the Keeping Properties and Composition of Butter.* Zeitsch. Nahr. Genussm., 1911, XXII, 553. (Analyst 1912, XXXVII, 52.)

C. Grimaldi, *The Influence of Preservatives on the Reichert-Meissl Value of Fats.* Chem. Zeit. 1908, XXXII, 794. (Analyst, 1908, XXXIII, 397.)

W. Friese. *The Estimation of Benzoic Acid in Margarine, Butter, and other Fats.* Pharm. Zentralhalle, 1911, LII, 1201. (Analyst, 1912, XXXVII, 92.)

G. Halphen. *The Detection of Benzoic Acid in Butter.* J. Pharm. Chim., 1908, XXVIII, 201. (Analyst, 1908, XXXIII 420.)

H. R. Richmond and J. B. P. Harrison. *The Rapid Estimation of Boric Acid in Butter.* Analyst, 1902, XXVII, 179.

H. R. RICHMOND AND E. H. MILLER. *Estimation of Boric Acid in Butter.* Analyst, 1907, XXXII, 144.

L. ROBIN. *The Detection of Benzoic Acid in Fats and especially in Butter.* Ann. Chim. Anal., 1908, XIII, 431. (Analyst, 1909, XXXIV, 18.)

RENOVATED BUTTER

C. B. COCHRAN. *The Detection of Renovated Butter.* J. Franklin Inst., 1899, CXLVII, 94. (Analyst, 1899, XXIV, 88.)

W. H. HESS AND R. E. DOOLITTLE. *The Detection of Renovated Butter.* J. Amer. Chem. Soc., 1900, XXII, 150. (J. Soc. Chem. Ind., 1900, XIX, 472.)

INFLUENCE OF FEEDING ON BUTTER

G. BAUMERT AND F. FALKE. *Alterations in the Character of Butter produced by Feeding with Fat.* Zeitsch. Nahr. Genussm., 1898; I, 665. (Analyst, 1899, XXIV, 6.)

H. T. CRANFIELD. *The Effect of Feeding with Coconut Cake and Linseed Cake on the Composition of Butter Fat.* Analyst, 1911, XXXVI, 445.

——. *The Effect of Feeding on the Composition of Butter: Decorticated Ground Nut Cake and Decorticated Cotton Cake.* Analyst, 1916, XLI, 336.

A. RUFFIN. *On the Influence of Feeding on some of the Constants of Butter.* Ann. Chim. Anal., 1899, IV, 383. (Analyst, 1900, XXVI, 70.)

M. SIEGFELD. *The Influence of Feeding with Coconut Cake and Beetroot Leaves on the Composition of Butter Fat.* Chem. Zeit., 1907, XXXI, 511. (Analyst, 1907, XXXII, 256.)

B. SJOLLEMA AND J. E. TULLEKEN. *Halphen's Reaction for Cottonseed Oil.* Zeitsch. Nahr. Genussm., 1902, V, 914. (Analyst, 1902, XXVII, 364.)

T. E. THORPE. *Experiments on the Effect on Butter of Feeding with Cottonseed and Sesamé Oil Cake.* Annual Report for Distribution of Grants for Agricultural Education in the Year 1897–8. (Analyst, 1898, XXIII, 255.)

J. WAUTERS. *The Detection of Cottonseed and Sesamé Oil in Fats.* Bull de l'Ass. belge Chim., 1899, XIII, 404. (Analyst, 1900, XXV, 125.)

BUTTER FAT

COMPOSITION OF BUTTER FAT

C. A. BROWNE, JUN. *Chemical Composition of Butter Fat.* J. Amer. Chem. Soc., 1899, XXI, 807. (Analyst, 1900, XXV, 38.)

O. HEHNER AND C. A. MITCHELL. *Stearic Acid in Butter.* Analyst, 1896, XXI, 329.

E. B. Holland, J. C. Reed and J. P. Buckley. *Estimation of Stearic Acid in Butter Fat.* J. Agric. Research, 1916, VI, 101. (Analyst, 1916, XLI, 209.)

Koefoed. *Composition of Butter Fat.* (Analyst, 1892, XVII, 130.)

Refractive Index

H. D. Richmond. *Temperature Correction of the Zeiss Butyro-Refractometer.* Analyst, 1907, XXXII, 44.

T. E. Thorpe. *Thermostat for Refractometer.* J. Chem. Soc., 1904, LXXXV, 257.

See also p. 129.

Reichert-Meissl Value

H. T. Cranfield. *On the Relation between the Reichert-Meissl, Kirschner and Polenske Values for Butter.* Analyst, 1915, XL, 439.

Official Method for the Test. Analyst, 1900, XXV, 309; *ibid.*, 1909, XXXIV, 514.

T. E. Thorpe. *Reichert-Meissl Values of English Butter Fat.* J. Chem. Soc., 1904, LXXIII, 254.

See also p. 130.

Coconut and Palm-kernel Oil in Butter

E. Avé Lallemant. *The Baryta Value of Butter Fat.* Zeitsch. Nahr. Genussm., 1907, XIV, 317. (Analyst, 1907, XXXII, 382.)

——. *Modification of the Method of König and Hart.* (Analyst, 1891, XVI, 139.)

J. Bellier. *Methods for the Analysis of Butter.* Ann. Chim. Anal., 1906, XI, 412. (Analyst, 1907, XXXII, 221.)

K. S. Caldwell and W. H. Hurtley. *The Distillation of Butter Fat, Coconut Oil, and their Fatty Acids.* Proc. Chem. Soc., 1909, XXV, 73.

R. K. Dons. *The Caprylic Acid Value of Butter Fat.* Zeitsch. Nahr. Genussm., 1907, XIV, 333. (Analyst, 1907, XXXII, 383.) (*Modification of Jensen's Method.* Analyst, 1905, XXX, 398.)

——. *Determination of the Caprylic Acid Value of Butter Fat.* Zeitsch. Nahr. Genussm., 1908, XV, 75. (Analyst, 1908, XXXIII, 122.)

E. H. Miller. *The Aldehyde Figure of Butter.* Analyst, 1912, XXXVII, 50.

E. Nockmann. *The Detection of Coconut Oil in Butter.* Zeitsch. Nahr. Genussm., 1911, XXI, 754. (Analyst, 1911, XXX, 451.)

C. Paal and C. Amberger. *Metallic Salts of the Volatile Acids in Butter Fat and Coconut Oil, and the Detection of Coconut Oil in Butter.* Zeitsch. Nahr. Genussm., 1909, XVII, 1. (Analyst, 1909, XXXIV, 99.)

See also Coconut Oil, p. 142.

VISCOSITY

G. F. WHITE AND R. H. TWINING. *The Viscosity of Butter Fat and its Substitutes.* J. Ind. Eng. Chem., 1913, V, 568. (Analyst, 1913, XXXVIII, 458.)

CHAPTER VIII

HARDENED OR HYDROGENATED OILS

A. BÖMER. *Hardened Oils.* Chem. Rev. Fett Ind., 1912, XIX, 221. (J. Soc. Chem. Ind., 1912, XXXI, 996.)

C. ELLIS. *The Hydrogenation of Oils.* J. Soc. Chem. Ind., 1912, XXXI, 1165.

K. BRAUER. *The Water Content of Margarines prepared from Hydrogenated Fats.* Zeitsch. öffentl. Chim., 1916, XXII, 209. (Analyst, 1917, XLII, 49.)

C. GRIMME. *Hardened Marine Animal Oils.* Chem. Rev. Fett Ind., 1913, XX, 129. (Analyst, 1913, XXXVIII, 373.)

——. *Colour Reactions of Hardened Whale Oil.* Chem. Rev. Fett Ind., 1913, XX, 155. (Analyst, 1913, XXXVIII, 433.)

R. H. KERR. *The Detection of Nickel in Fats.* J. Ind. Eng. Chem., 1914, VI, 207. (Analyst, 1914, XXXIX, 254.)

J. KLIMONT AND K. MAYER. *Use of Hydrogenated Fish Oil in the Manufacture of Margarine.* Zeitsch. angew. Chem., 1914, XXVII, 645. (J. Soc. Chem. Ind., 1915, XXXIV, 148.)

A. W. KNAPP. *Note on Hardened Oils.* Analyst, 1913, XXXVIII, 102.

H. KREIS AND E. ROTH. *Solidified Oils and the Detection of Arachidic Acid.* Zeitsch. Nahr. Genussm., 1913, XXV, 81. (Analyst, 1913, XXXVIII, 160.)

W. NORMANN AND E. HUGEL. *Analysis of Hardened Oils.* Chem. Zeit., 1913, XXXVII, 815. (Analyst, 1913, XXXVIII, 432.)

H. T. OFFERDAHL. *The Production and Utilisation of Whale Oil.* Ber. deut. Pharm. Ges., 1913, XXIII, 558. (J. Soc. Chem. Ind., 1914, XXXIII, 32.)

P. SABATIER AND J. C. SENDERENS. Comptes rend., 1900, CXXX, 723; CXXXI, 187.

A. E. SANDELIN. *Hydrogenerated Fats.* Technikern, 1913, 350. (J. Soc. Chem. Ind., 1914, XXXIII, 1097.)

M. TORTELLI AND E. JAFFE. *Specific Colour Reactions of Marine Animal Oils and their Hydrogenated Products.* Annali Chim. Applic., 1914, II, 80. (Analyst, 1915, XL, 14.)

CHAPTER IX

MANUFACTURE OF MARGARINE

BUTTER AND MARGARINE ACT, 7 Ed. VII, c. 21. Analyst, 1907, XXXII, 399.

OFFICIAL REPORT: *The Margarine Clause of the Food and Drugs Act.* Analyst, 1900, XXV, 309.

W. ARNOLD. *The Butter Fat Content of Margarine.* Zeitsch. Nahr. Genussm., 1914, XXVII, 379. (Analyst, 1914, XXXIX, 216.)

C. H. CRIBB AND P. A. E. RICHARDS. *Notes on the Analysis of Margarine.* Analyst, 1911, XXXVI, 327.

K. JENSEN. *The Detection of Coconut Oil in Margarine.* Farmaceutisch. Tidende, 1905, 385. (Analyst, 1905, XXX, 396.)

A. KIRSCHNER. *Determination of Butter Fat and Coconut Oil in Margarine.* Zeitsch. Nahr. Genussm., 1905, IX, 65. (Analyst, 1905, XXX, 205.)

M. MONHAUPT. *Estimation of Butter Fat in Margarine in the Presence of Coconut Oil.* Chem. Zeit., 1909, XXXIII, 305. (Analyst, 1909, XXXIV, 212.)

A. PARTHEIL. *On the Addition of Dimethylazobenzene to Margarine to afford Evidence of Identity.* Chem. Zeit., 1897, XXI, 255. (Analyst, 1897, XXII, 157.)

VON RAUMER. *On the Compulsory Addition of Sesamé Oil to Margarine.* Zeitsch. angew. Chem., 1897, 749. (Analyst, 1898, XXIII, 7.)

L. SETTIM AND L. MAURANTONIO. *The Detection of Vegetable Oils in Margarine.* Ann. Lab. Chim. Gabelle, 1912, VI, 203. (Analyst, 1913, XXXVIII, 21.)

See also COCONUT OIL *and* BUTTER

SUBJECT INDEX

NAME INDEX

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY & SONS, LIMITED,
BRUNSWICK ST., STAMFORD ST., S.E. 1,
AND BUNGAY, SUFFOLK.